

Synthesis of Sugars by Hydrolysis of Hemicelluloses- A Review

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1. INTRODUCTION

The biorefinery concept involves transforming biomass to energy, materials, and chemicals.^{1,2} Potential raw material

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sources are plant materials, about 180 billion tons of which are produced annually,³ out of which 40% is cellulose⁴ and about 30% hemicelluloses.⁵ One method to obtain primarily sugars is acid hydrolysis.⁴ There are several other methods to perform this step, such as hot⁶ and supercritical water treatments,⁷ alkaline treatment,⁸ ammonia fiber explosion or expansion (AFEX),⁹ steam explosion,⁹ COSLIF,^{10–12} or the use of ionic^{13–15} and supercritical liquids as solvents. A common drawback in many of these processes is the instability of sugars, since sugars are easily dehydrated and further transformed to small molecular weight degradation products. This is the case in hot and supercritical conditions when cellulose dissolution suffers from low selectivity,⁷ whereas it should be pointed out that sugar degradation is very minor in COSLIF and AFEX, as well as in low-temperature processes with ionic liquids. Despite the fact that glucose can be dehydrated in acid hydrolysis of glucans using concentrated mineral acids, it has been reported that glucan hydrolysis with fuming HCl was possible at 0 °C followed by extraction with the main product being glucose.¹⁶

The acid hydrolysis of biomass for production of sugars has been studied intensively for 100 years.^{4,17–142} Acid hydrolysis of cellulose was recently reviewed alone.^{4,143} Cellulose hydrolysis with concentrated mineral acids is not an example of green chemistry, because of the abundance of salts formed during the neutralization step. Furthermore, the spent acids should be disposed of, and the equipment costs are high, since some strong acids (H₂SO₄, HCl) are very corrosive at high temperatures. The concentration of concentrated sulfuric acid (95–98%) is very high being 18 mol/L, whereas phosphoric acid concentration is lower being in the range of 0.1–1 mol/L for 76.1–91.7% solutions (aqueous phosphoric acid contains typically 85% phosphoric acid). When mild organic acids are used, high temperatures are needed and the selectivity drops easily due to sugar dehydration. Cellulose, which is a partially crystalline material consisting of glucose units linked with each other via β -bonding between two glucose units together with inter- and intramolecular hydrogen bonds in crystalline cellulose,⁴ is more difficult to depolymerize than hemicelluloses, which are heteropolysaccharides of two or more different types of sugar units. Furthermore, neutralization of salts is not needed when new dissolution methods for biomass are used, such as application of ionic liquids.

In selective acid hydrolysis of hemicelluloses with diluted acids, the aim is to release most of the easily released sugars from hemicellulose and cellulose and try to keep most cellulose and lignin intact. This implies that the acid hydrolysis parameters, such as temperature, acid concentration, and concentration of the biomass should be optimized. At too high temperatures, undesired side reactions take place, and the process is not selective due to the dissolution of lignin and cellulose. It should be pointed out here, however, that dissolution of lignin is very difficult. The presence of aromatic compounds from dilute acid treatment inhibits, for example, microbial transformation of xylose to xylitol.¹⁰⁹

The majority of the literature reports on acid hydrolysis of biomass or waste aim at enzymatic hydrolysis and ethanol fermentation of sugars.¹⁴⁴ Since acid hydrolysis of hemicelluloses is easier than that of cellulose, it is performed as a pretreatment step for biomass,^{19,20,38,46,52,54–60,69,71,74,81,83,84,87–90,92,93,97–100,105,113,126} followed by enzymatic or high-temperature acid hydrolysis of the residue, such as cellulose. Thereafter, the fermentable sugars are transformed to bioethanol.¹⁴⁵ Subsequently, enzymes can be

separated easily, at low cost, from soluble sugars by adsorption for further hydrolysis.¹⁴⁶

Sugars, generated from acid hydrolysis of hemicelluloses, are valuable products and intermediates for synthesis of pharmaceuticals and health-promoting agents.¹⁴⁷ The most abundant sugars in nature are D-glucose, D-fructose, D-galactose, and D-mannose (hexoses), as well as D-xylose, L-arabinose, and D-ribose (pentoses).¹⁴⁸ Some of the naturally occurring rare sugars appear in relatively large amounts in wood biomass, as well as in agricultural and pulping wastes. Rare sugars are defined according to the International Society of Rare Sugars as monosaccharides and their derivatives, which rarely occur in nature.¹⁴⁹ Rare sugars are present in hemicelluloses, which comprise about 30% of the woody biomass. The rest is mainly cellulose, lignin, and extractives.

Sugars from hemicelluloses are easy to separate almost quantitatively from the lignocellulosic biomass^{54,57,91} due to their structures and because they usually are noncrystalline. After dilute acid hydrolysis of biomass, a solid waste, containing cellulose and lignin, can be separated by filtration.⁹¹ When sugars are produced from biomass, there are, however, several steps required to obtain pure sugars. The sugar-containing hydrolysate is neutralized after acid hydrolysis. Thereafter, the formed salt, such as gypsum¹¹⁰ or barium sulfate⁸² if sulfuric acid was used as a catalyst, should be filtered.¹¹⁰ It should be pointed out here that if organic acids are used, they can be evaporated, thus avoiding the neutralization step, and no solid waste is formed.⁵² Thereafter, the monomeric sugars can be separated to different sugar fractions with the aid of chromatographic techniques.^{107,110,150,151} The separation is facilitated by using different types of anionic or cationic exchanger resins. Additionally, rare sugars will be decolorized by active carbon,⁸² filtered, and concentrated⁷⁷ and finally crystallized from the hydrolysates.^{78,82,110} Sometimes antisolvents, such as acetone,⁷⁴ are used to precipitate impurities. Furthermore, lignin is soluble in organic solvents¹⁵² thus retaining sugars in water solution.⁷⁷ After crystallization, different rare sugars can be further transformed to different valuable derivatives. It should be pointed out here that the separation methods for rare sugars using dilute acid hydrolysis are not yet very developed, since several different separation and filtration, reconcentration steps,^{76,77} and purifications and crystallization of sugars should be performed. The downstream processing of sugar containing streams remains still a challenge for further research.

The aim of this work is to review the state-of-art in selective acid hydrolysis of lignocellulosic material to produce the most utilized rare sugars that can be derived directly from biomass, such as xylose, mannose, galactose, arabinose, and rhamnose. Currently sugars derived from hemicelluloses are not used as raw materials, for example, in kraft pulping processes, but instead they are burnt as a part of black liquor to produce energy. Structures and sources of cellulose and hemicelluloses are reviewed in section 2. There are several rare sugar products already on the market, such as mannose and xylitol. For instance, mannose is used as such for urinary track diseases. Xylitol, which is produced via catalytic hydrogenation¹⁵³ or microbial conversion,¹⁵⁴ has several beneficial features, such as anticaries, antiinflammatory, and sweetening properties. More examples of applications of rare sugars are given in section 3. In addition to the above-mentioned rare sugars, there are also other rare sugars, which are not reviewed in this work. The utilization of sugar alcohols, also sorbitol and mannitol, which are the main products from one-pot transformation of cellulose to sugar alcohols over heterogeneous catalysts, is reviewed also in section 3.

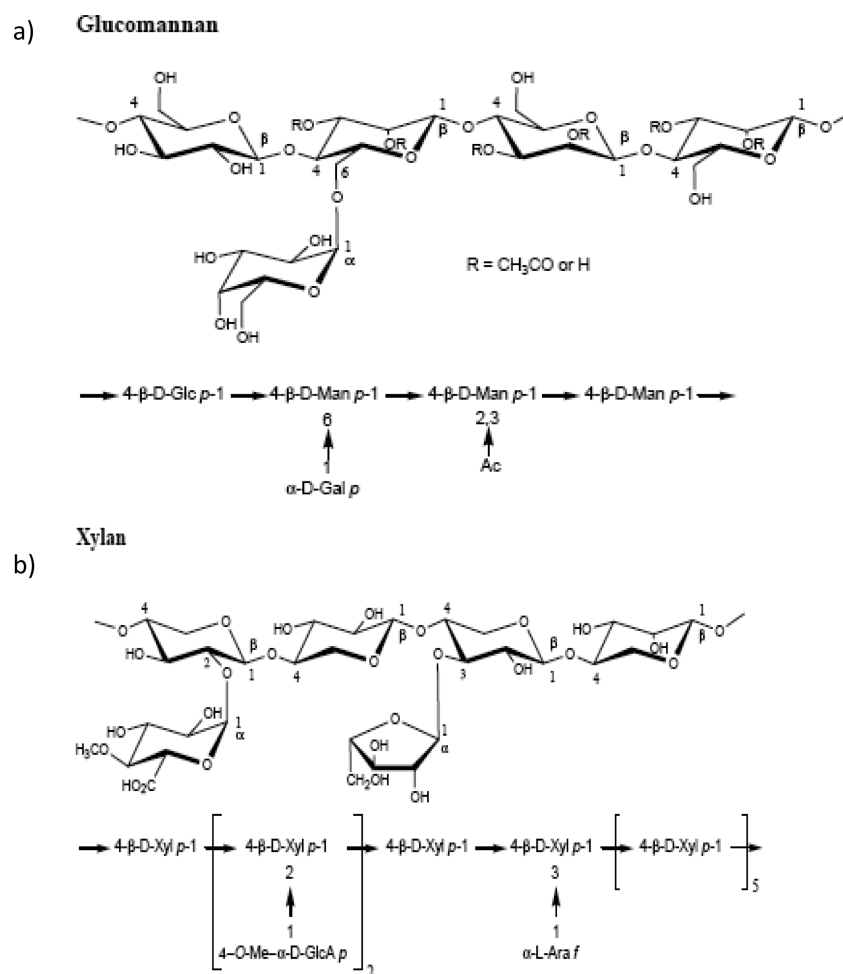


Figure 1. The most important hemicelluloses of softwood: (a) glucomannan and (b) xylan.¹⁶⁹

The acid hydrolysis of biomass to produce rare sugars is discussed in sections 4–7. Selective acid hydrolysis of hemicelluloses to produce sugars has been scarcely reviewed in the literature despite the huge number of publications reporting dependencies of different parameters on the hydrolysis activity and selectivity. There exist only two reviews comprising and discussing acid hydrolysis of cellulose and hemicelluloses mainly reporting on reactor selection and kinetic modeling,^{111,116} whereas no systematic reports exist on the type of raw materials, effect of acid type and concentration, etc. In addition, the acid hydrolysis of inulin has also been reported here for comparative purposes,⁹⁵ although it does not form a rare sugar, since it is composed of fructose units. The kinetics of the acid hydrolysis is presented in section 5. The main parameters in dilute acid hydrolysis are temperature, dissolution time, acid, and solid to liquid ratio. The reported values for apparent activation energies and reaction orders are reviewed here. Furthermore, acid hydrolysis using model compounds as feedstocks has also been reported in this review to give more information about the reaction mechanism.^{31,101} The mechanism of acid hydrolysis of hemicelluloses is presented in section 6 and kinetic modeling of acid hydrolysis in section 7. The aim in this review was to systematically report all the kinetic regularities and structural characteristics of the raw material affecting the selective acid hydrolysis of hemicelluloses for synthesis of rare sugars. These processes have a potential to provide raw material for dietary fibers,^{76,80,89,95,102} food additives,¹⁴¹

health-promoting agents,¹⁰⁹ sweeteners,^{62,73–75,85,86,102,109,118,121} and pharmaceuticals.^{75,77–79,82,86,102,107,141} The acid hydrolysis of cellulose is not in the main focus in the work; moreover coverage of this topic is limited mainly to the last 10 years of studies. On the other hand, acid hydrolysis of hemicelluloses and cellulose has been compared, since there are differences between these two processes, which originate from the differences in the structures of hemicelluloses and cellulose. Different processes for wood saccharification are briefly reviewed in section 8.

2. CELLULOSE AND HEMICELLULOSES

Cellulose is the most abundant biomaterial in nature. Hemicelluloses are present also in relatively large amounts in plants, about 20–30 wt % of the total mass, and they exist closely associated with cellulose and lignin. The chemical composition and structure of cellulose and hemicelluloses are reviewed below.

2.1. Cellulose

Cellulose is a homopolysaccharide composed of D-glucose units linked to each other via β-1,4-glucosidic bonds.¹⁵⁵ The repeating unit in cellulose is anhydrocellobiose.¹⁵⁶ Cellulose is a semicrystalline polymeric material containing both crystalline and amorphous regions. The degree of polymerization varies depending on the type of raw material in a range of 100–20000.¹⁵⁷ Native cellulose is in the structure cellulose I,¹⁵⁸ although seven polymorphs

Table 1. Distribution of Different Hemicelluloses in Wood in wt %¹⁶⁷

hemicellulose	hardwood	softwood
methylglucuronoxylans	80–90	5–15
arabinomethylglucuronoxylans	0.1–1	15–30
glucomannans	1–5	1–5
galactoglucomannans	0.1–1	60–70
arabinogalactans	0.1–1	1–15
other galactans	0.1–1	0.1–1
pectins	1–5	1–5

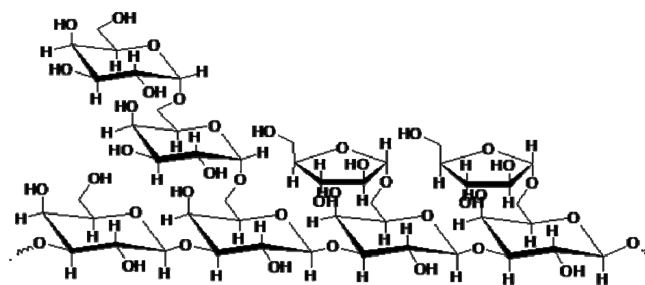
of cellulose are known (I_{α} , I_{β} , II, III_I, III_{II}, IV_I, IV_{II}).⁴ In nature, crystalline cellulose is found as I_{α} and I_{β} .^{159,160} I_{α} is present, for example, in cell walls of algae, whereas I_{β} is found in cotton and ramie fibers.⁴ During dissolution and swelling, cellulose I transforms to cellulose II,¹⁵⁵ but cellulose III is also formed from cellulose I by ammonia treatment. Furthermore, cellulose IV can be prepared by treating cellulose III with glycerol.¹⁵⁵ Thermodynamically, the most stable form of cellulose is cellulose II.¹⁶¹ In acid hydrolysis, the amorphous cellulose is quickly hydrolyzed, whereas the dissolution of crystalline cellulose is limited by the limited access of reactants to β -1,4-glycosidic bonds.¹⁶² Furthermore, water is absent from the crystalline regions of cellulose.¹⁵⁶ The crystallinity is caused by the presence of inter- and intramolecular hydrogen bonds between different anhydroglucan chains. It has been stated that if the number of hydrogen bonds making inter- and intramolecular bonds in I_{α} cellulose is 8 per repeating unit, the structure is crystalline, but if it is 5.3, the structure is amorphous.^{156,163}

The crystalline structure in cellulose is very stable.¹⁶⁴ Several attempts have been performed to transfer crystalline cellulose to an amorphous one, such as with physical (ball milling, grinding, steaming) and chemical treatments (alkali, acid, gas, oxidation), which will in turn decrease the degree of polymerization and increase the number of reducing end groups.¹⁵⁶ A proposed method is to treat cellulose with phosphoric acid to increase its surface area.^{165,166} The treatment of microcrystalline cellulose with an acid did not, however, decrease the degree of polymerization.¹⁶⁶ This method was applied as a pretreatment method, when the effect of crystallinity was systematically studied on hydrolysis of cellulose, see section 5.8.

2.2. Hemicelluloses

2.2.1. Hemicelluloses in Wood. Hemicelluloses are heteropolysaccharides composed of different sugar units, the major hemicelluloses being mannans, xylans, arabinans, and galactans.¹⁶⁷ The most important hemicelluloses in softwoods (coniferous trees) are galactoglucomannans (20%) and arabinoglucuronoxylans (10%) (Figure 1).^{168,169} Furthermore, softwoods contain arabinogalactan, xyloglucans, and other glucans. Pine (*Pinus sylvestris*) and spruce (*Picea abies*) contain about 20 wt % O-acetyl-galactoglucomannan and 5–10 wt % arabino-4-O-methyl glucuronoxylan.¹⁷⁰ The amounts of different hemicelluloses in wood are listed in Table 1.^{167,170–173}

The most important hardwood hemicellulose is xylan, especially O-acetyl-4-O-methylglucuronoxylan, amounting to about 80–90% of the hardwood hemicelluloses.¹⁶⁷ Hardwoods contain acetylglucuronoxylan in about 15–30 wt % of the dry weight¹⁷⁴ without any arabinose side chains opposite to softwood

**Figure 2.** Structure of arabinogalactan adapted from ref 79.

xylans. Another hemicellulose in hardwood is glucomannan. The structures of hardwood xylans are shown in Figure 1b.

Arabinogalactans are more abundant hemicelluloses in softwoods than in hardwoods,¹⁶⁷ with amounts in the range of 1–15% for softwood and 1–5% for hardwood, respectively. Arabinogalactans can be extracted from Western (*Larix occidentalis*) and Siberian (*L. sibirica*) larch heartwood. Typically the ratio between galactose to arabinose is 6:1¹⁷⁵ in arabinogalactan (Figure 2). The polymer chain is highly branched with β (1,3) and β (1,6) units between galactose units and small amounts of glucuronic acid units.¹⁷⁶

2.2.2. Hemicelluloses in Pulping Liquors. Hemicelluloses are produced as a byproduct in kraft pulp mills, but they are not optimally utilized.⁸³ In order to make the kraft process economically more attractive, pre-extraction of hemicelluloses can be performed. This step decreases the solid fiber yield only to a minor extent.¹⁷⁷ Furthermore, partially recovered pulping liquor, green liquor, can be used as an extraction solvent in the prepulping. Green liquor also contains salts, which have a buffering action and prevent the pH from dropping too much, which in turn would reduce the pulp properties. Additionally, xylose can also be produced from the alkaline extract of bleached hardwood pulp using the following steps: (1) concentration of the hydrolysate with nanofiltration; (2) neutralization of the hydrolysate; (3) acid hydrolysis with diluted sulfuric acid.¹⁷⁸ In typical processes, there are several steps, in which hemicellulose fractions are separated prior to acid hydrolysis, for example, xylans are precipitated by alcohol and separated chromatographically to recover pure xylan.¹⁷⁹

Thermomechanical pulping waste waters contain also galactoglucomannans, which could to be recovered in amounts of about 5 kg per ton of pulp.¹⁸⁰ It is not, however, currently isolated for industrial use. O-Acetyl-galactoglucomannans are composed of randomly distributed (1,4)-linked β -D-mannopyranosyl and (1,4) linked β -D-glucopyranosyl units with α -D-galactopyranosyl units as side units to mannosyl units. Galactoglucomannan contains O-acetyl groups on every second mannose unit on average.

2.2.3. Hemicelluloses in Plant Gums and Plants. High arabinose contents have been found in certain plant gums, such as gum arabic.¹⁰² The major fraction of gum arabic consists of a highly branched polysaccharide β -(1,3)-linked galactose backbone with branches of arabinose and rhamnose. The branches terminate in glucuronic acid.¹⁸¹ Rhamnose can also be selectively produced by hydrolysis of gum arabic (see section 4.3.5).⁷⁷ In addition to hemicelluloses, rhamnose is also found in nature in glycosides containing a sugar unit combined with a nonsugar unit. Examples of rhamnose-containing glycosides are such as rutin, hesperidin, quercetin, myricitin, and naringin, which are flavonoids, and thus their hydrolysis is outside the scope of this

review. Inulin, which occurs in several plants, is a poly((2→1)- β -D-fructofuranan),^{182,183} and its acid hydrolysis has been investigated in ref 95 (see section 5).

2.2.4. Hemicelluloses in Agricultural Wastes. There are several types of agricultural wastes used as raw materials for acid hydrolysis to produce sugars, for example, sugar cane bagasse, sugar beet pulp, rice and wheat straw, cornstalk and cobs, etc. Agricultural waste contains typically 30–42% cellulose, 20% xylan, and 20–27% lignin.¹⁴¹ Furthermore, sunflower stalk and cotton seed cake as a source of biomass are discussed here. In this section, their availability and chemical composition is reviewed, while their hydrolysis to produce xylose is discussed in section 4.3.1.

Sugar cane bagasse is a valuable feedstock, since more than 70% of its dry mass is carbohydrates.¹²¹ It is rich in xylan, about 20.6 wt %.⁹¹ Sugar cane bagasse contains hemicelluloses with a xylan backbone to which arabinose and glucuronic acid groups are linked.¹⁸⁴ Furthermore, the cellulose concentration in sugar cane bagasse is lower than that in wood chips,¹⁸⁵ being more prone to hydrolysis (see section 4.3.1). Currently sugar cane bagasse is either used as a boiler fuel⁸⁹ or alternatively not utilized but regarded as an environmental problem.⁷² There is much interest in transforming it to monomeric sugars and further ferment the sugars to ethanol.⁸⁹

Large amounts of polysaccharides are achieved from sugar beet, from which sucrose is removed by extraction.¹⁰² The sugar beet pulp contains about 55% hemicelluloses (including most probably pectins), whereas the cellulose and lignin contents are about 22 wt % and 2 wt %, respectively.⁴⁴ This pulp is composed of galacturonic acid polymers, in which the polymer has backbone regions containing rhamnose and galacturonic acid, typical for plant pectins. Additionally, arabinan and galactan polymer chains are connected to the rhamnose units.¹⁰⁷ The sugar beet pulp contains about 21% arabinose.¹⁶⁸ One component is arabinan, which is built up from L-arabinose groups linked via (1,3)- α - or (1,2)- α -linkages or both. Arabinan is a hemicellulose obtained via treatment of sugar beet pulp with aqueous lime and can be hydrolyzed to produce L-arabinose.^{110,186} If pectin recovery is desired, it can be hydrolyzed first at pH 1.5 at 70 °C with acetic acid from sugar beet pulp and precipitated with isopropanol. Thereafter, the arabinose present in the filtrate can be separated via chromatographic techniques.¹⁰⁷

Rice straw, a side product from rice production with total annual capacity of 800 million dry tons,¹⁴⁵ contains 32% cellulose, 24% hemicelluloses, and only 13% lignin.¹⁸⁷ The polymeric composition of rice straw is the following: glucan 43%, xylan 20%, arabinan 2.7%, lignin 17%, and ash 11%.⁸⁵ Currently rice straw is burnt or incorporated in the soil. The former alternative is environmentally harmful, producing CO₂, CO, and CH₄ emissions.¹⁴⁴ Furthermore, due to the low energy and protein content of rice straw, it is suitable neither for combustion nor for animal feed.⁸⁶ The energy value of straw is 17.6 MJ/kg compared with 44.2 MJ/kg, which is the energy value of heating oil.¹⁸⁵ Rice straw is easy to hydrolyze with dilute acids, since its lignin content is low.

Wheat straw, available in large quantities¹⁸⁸ in, for example, the US, contains arabinoxylans, in which xylose units linked via β -(1,4)-glycosidic bonds and arabinose residues are attached to the main chain.¹⁸⁹ Typically wheat straw contains only 24% cellulose, about 20% lignin, and 21% hemicelluloses together with 28% ash, waxes, and low-molecular weight carbohydrates. The rest of wheat straw is starch and protein,¹⁹⁰ and thus due to

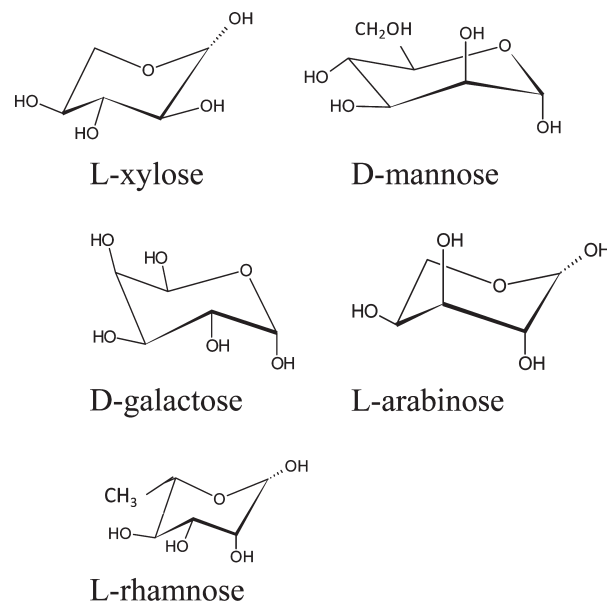


Figure 3. Five commercially important rare sugars.

the low cellulose content, selective dilute acid hydrolysis of arabinoxylans from wheat straw can be performed at relatively low temperatures (see section 4.3.1).⁵⁶

Cornstalk and corncobs are agricultural wastes with a low content of lignin.¹⁷⁵ For example, corn stalk contains about 3% lignin, but it is rich in cellulose and hemicelluloses, their amounts being 29% and 28%, respectively.¹⁹¹ Corn stover is a waste that contains on average about 20% xylan and 3% arabinan,⁸⁰ whereas its cellulose and lignin contents are only about 35% and 17%, respectively.¹⁹² Sunflower stalk is also a waste formed during the sunflower seed production, and it contains cellulose, hemicelluloses, and lignin at about 38%, 30%, and 11%, respectively.³⁰ Typically the stalk to seed weight ratio is about 2.3.¹⁹³ Large amounts of sunflower stalk are produced, for example, in Spain.³⁰ Vegetable fibers, such as envelopes of corn grains, contain large amounts of arabinoxylan similar to wheat straw (see above).⁷⁶ One source of xylan is cotton seed residual cake, which contains after delignification only xylan and uronic acid, and its sugar content is 75%.⁶⁸ It has been prepared by soaking cotton seed in sodium hypochlorite solution to remove lignin, followed by washing with water.⁶⁸

D-Galactose can be obtained from cashewnut shells, which is an industrial waste material after removal of kernel, especially in India.¹⁹⁴ Water-soluble polysaccharides can be prepared from cashewnut shells according to the method described in ref 195.

3. VALUE-ADDED PRODUCTS FROM RARE SUGARS AND SUGAR ALCOHOLS

The most important utilization of sugars is related to production of biofuels, such as ethanol¹⁹⁶ and hydrogen^{197–199} via fermentation. Synthesis of biofuels is only shortly reviewed here, since the main focus of the review is in utilization of rare sugars to produce value-added chemicals.

There are several enzymes able to convert hexoses to bioethanol but unable to process pentoses.¹⁹⁶ It was also stated¹⁹⁶ that the utilization of hemicellulose to produce ethanol is still a challenge, since the enzymes used for this purpose are sensitive to inhibitors and exhibit low ethanol tolerance. Thus it has been proposed that

hemicellulose would be used for production of biohydrogen.¹⁹⁶ Therefore, one of the future biorefinery concepts can rely on producing multibiofuels from biomass, such as bioethanol from cellulose, biohydrogen from hemicellulose and biogas from the effluents of bioethanol and biohydrogen production.¹⁹⁶ For the formation of biohydrogen, typically mild acid biomass hydrolysis has been carried out followed by enzymatic hydrolysis of the solid residue.¹⁹⁷ After hydrolysis, the hydrolysates and the dissolved sugars from residues washed with water have been fermented by aid of thermophilic bacteria to produce hydrogen. Very high hydrogen yields have been obtained from fructose, sorbitol, and D-glucose using *Escherichia coli* DJT135 enzyme.¹⁹⁹ The challenge of using mild acids in biomass hydrolysis is the simultaneous production of fermentation inhibitors, such as 5-hydroxymethylfurfural and furfural.¹⁹⁷

The most important commercially utilized rare sugars are xylose, mannose, galactose, arabinose, and rhamnose (Figure 3), which all can be prepared via acid hydrolysis of biomass. These rare sugars have several potential application areas, which are briefly reviewed in ref 145. In particular, they are applied in the pharmaceutical industry and as sweeteners and food additives. Below, the current and potential application areas of these rare sugars and their derivatives are given in more detail.

3.1. Products from Rare Sugars and Their Derivatives

3.1.1. L-Xylose. L-Xylose can be hydrogenated or enzymatically transformed to xylitol, which is a sweetening agent and is also used for preventing tooth decay,^{85,200,209} as well as acute otitis.^{85,201} Typically xylose hydrogenation is performed in a temperature range of 80–130 °C using Raney nickel as catalyst in water solutions under 40–70 bar of hydrogen.^{153,202} Another catalyst applied in xylose hydrogenation is ruthenium.²⁰³ The reaction is very selective, and only traces of other products, such as furfural, are formed. Xylitol can alternatively be produced via enzymatic transformation using immobilized D-xylose isomerase of *Bacillus coagulans* or immobilized cells of *Mycobacterium smegmatis*²⁰⁴ or using *Candida guilliermondii* yeast.⁸⁶

3.1.2. D-Mannose. D-Mannose has applications in production of pharmaceuticals and can also act as a growth accelerator for swine.²⁰⁵ A valuable derivative of D-mannose is D-mannitol, which is produced via catalytic hydrogenation of either D-mannose or fructose.²⁰⁶ It is also obtained as a secondary product from hydrolytic hydrogenation of cellulose. D-Mannitol has several similar applications as xylitol, such as being a constituent in a natural deodorant²⁰⁷ and in tablets as fast-dissolving sugars,²⁰⁸ exhibiting anticarcinogenic activities,²⁰⁸ and as bulking agents in therapeutic agents.²¹⁰ Furthermore, mannitol has the potential to act as a cough-provocation test in nonasthmatic chronic cough.¹⁹⁵

D-Mannose is already available as a product to decrease the symptoms of lower urinary track diseases. This sugar is absorbed in the human body more slowly than glucose, and thus it is transferred directly to the blood circulation. It can be fixed with bacteria, such as *E. coli*, thus removing bacteria from the human body.²¹¹ An advantage of D-mannose is that it can be used together with antibiotics. D-Mannose can also decrease the sugar and triglyceride levels in diabetic patients. Mannose is also used as an indicator for the presence of a commonly used phosphomannose isomerase (PMI) gene.

One way to produce mannose from glucose is an enzymatic isomerization of glucose using an extracellular glucose isomerase of *E. coli*, through so-called Lobry–de Bruyn–van Ekenstein

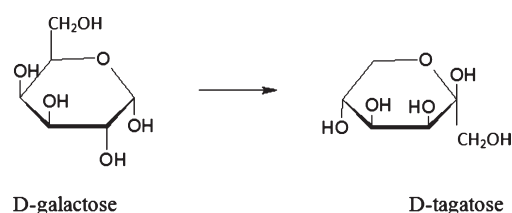


Figure 4. Isomerization of D-galactose to D-tagatose.

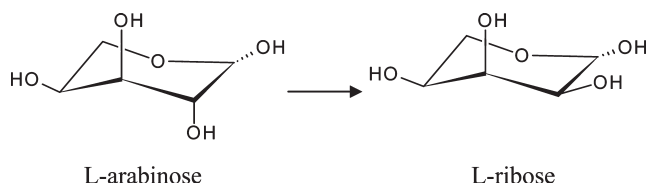


Figure 5. Epimerization of L-arabinose to ribose over molybdenum compounds.

transformation path from D-glucose to D-fructose, further transformation to D-mannose.²¹² This possibility can make the acid hydrolysis of O-acetylgalactoglucomannan economically more interesting (see section 4.3.2). Furthermore, D-mannitol can be produced by catalytic hydrogenation of fructose.²¹³

3.1.3. D-Galactose and Other Rare Sugars Derived from Galactose. Galactose has many applications in pharmaceutical and food related areas. It is, for example, used as nutrient medium for maintaining viability of neural cells.²¹⁴ Furthermore, galactose has been used in drugs exhibiting cytotoxic and anti-inflammatory properties.²¹⁵

D-Galactose can be epimerized to D-tagatose¹⁶⁷ using borates (Figure 4) with yield of 77% when borate buffer is utilized. In addition to borates, also arabinose isomerization can be used in lieu of borates to epimerize D-galactose into D-tagatose.

The biological and toxicological properties of D-tagatose have been reviewed in ref 216. Tagatose exhibits prebiotic properties, and thus it has several application areas, such as food sweetening. It can also be used by diabetic patients, for inhibiting dental caries,²¹⁷ for treatment of hyperglycemia, anemia, and hemophilia, and as an agent to improve fetal development.²¹⁸ Furthermore, D-tagatose is applied as a food additive²¹⁶ and as a low-calorie sweetener.²¹⁸

Galactose can also be transformed to L-fucose,²¹⁴ a deoxy sugar, which is present also in spent liquors from pulping processes.¹⁵¹ Hemicellulose hydrolysate from birch wood contains both fucose and rhamnose in L-form.¹⁵¹ Fucose can be separated from other sugars by chromatographic separation techniques. L-Fucose has several applications in cosmetics, since it exhibits an effect to maintain the level of moisture in the skin.¹⁵¹ Furthermore, L-fucose can exhibit anticarcinogenic and immunomodulating properties and thus be used for treatment of inflammations.²¹⁹ L-Fucose has also potential applications in treating tumors and disorders related to the human immune system¹⁵¹ and has even been used in anti-HIV applications.²¹⁹

Galactitol, the sugar alcohol of galactose, is prepared by catalytic hydrogenation of galactose. It can be used as a carrier for therapeutic agents.²²⁰ Furthermore, galactitol can be dehydrated by using mineral acids to prepare 1,4-anhydro-galactitol, which is used as a low-calorie agent in food.²²¹

3.1.4. L-Arabinose and L-Ribose Prepared from L-Arabinose. L-Arabinose has been applied as a noncaloric sweetener, as

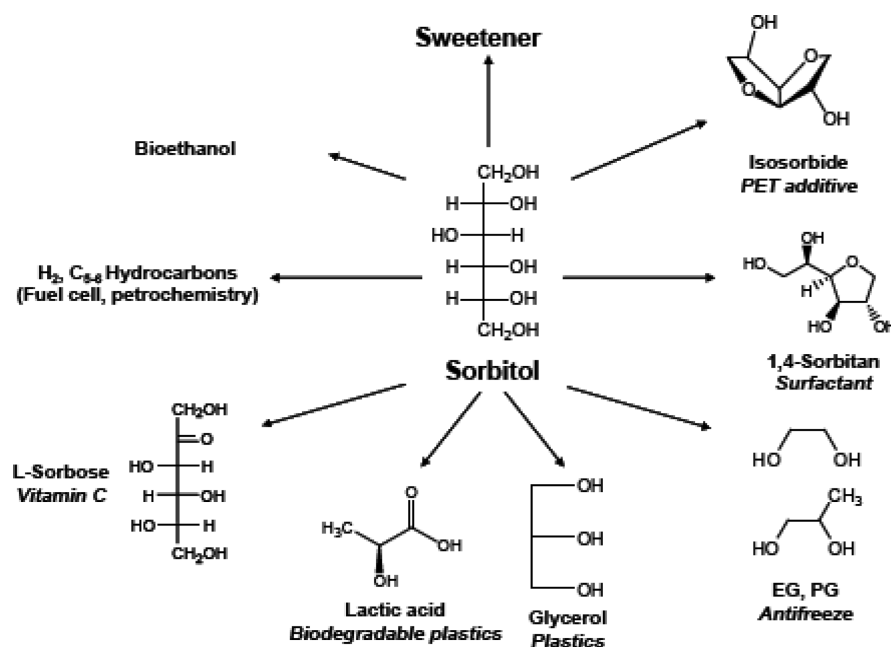


Figure 6. Different products obtained from sorbitol.¹⁷ Reprinted with kind permission from Springer Science & Business Media.

a dietary fiber, in flavors, and as an intermediate for synthesis of drugs. The property, as a noncaloric sweetener is associated with its inability to be metabolized in animals.⁷⁵ It inhibits the absorption of sucrose²²² and at the same time prevents high glucose levels in blood. When L-arabinose was added to sucrose, the sucrose digestion was reduced by 60%, and thus L-arabinose and sucrose act similarly to dietary fibers.⁷⁵ L-Arabinose is used in treating diabetes²²³ and hyperglycemia²²⁴ and also exhibits antiviral properties.

L-Arabinose can be chemically epimerized to L-ribose in the presence of molybdenum compounds^{225,226} or by using xylose isomerase²²⁷ as a catalyst (Figure 5). The chemical epimerization is performed by using H_2MoO_4 as a catalyst in water at 95 °C.²²⁵ The yield of L-ribose was 54% after 3 h.

L-Ribose can be used as a chiral starting material for synthesis of L-nucleoside based drugs, especially benzimidazole ribosides,²²⁸ which exhibit antiviral, antimalarial, antihypertensive, and anticancer activities.²²⁹ Furthermore, there are already ongoing clinical trials for using L-ribose as a potential anti-HIV and anti-HCV pharmaceutical agent.²²⁸

3.1.5. L-Rhamnose. L-Rhamnose is used in cosmetics as well as in pharmaceuticals. In cosmetic products, it has a role of preserving the skin moisture level analogous to L-fucoses. L-Rhamnose can be transformed to 5-deoxy-L-ribose, which has some medical applications.²³⁰ Deoxy sugars are L-nucleoside analogues, which can be used for treatment of viral diseases.²³¹ It has also been reported that L-rhamnose inhibits the adsorption of bacteriophage to cells.²³²

3.2. Products from Sorbitol

The best and simplest way to obtain sorbitol is through hydrogenation of glucose on Ni or Ru catalysts. Alternatively, it can be selectively produced via hydrolytic hydrogenation of cellulose. Sorbitol has several application areas, acting analogously to xylitol and mannitol as a sweetener and as a starting material for vitamin C synthesis. In addition to these applications, there are also other chemicals derived from sorbitol, such as sorbitan, glycols, glycerol, lactic acid, and sorbose (Figure 6).¹⁷ Sorbitol has been

selected as one of the top 12 value-added products from biomass in the recent US DOE report²³³ due to its potential to be used as hydrogen and hydrocarbon source for fuels.

4. ACID HYDROLYSIS OF LIGNOCELLULOSIC MATERIALS AND HEMICELLULOSES FOR PRODUCTION OF SUGARS

Acid hydrolysis of cellulose is old chemistry. It is still far from green, although there exists a few pilot or industrial scale processes of acid hydrolysis of cellulose to produce bioethanol.²³⁴ The most severe problems in this process arise from corrosion and waste elimination, as well as from the low selectivity.²³⁵ In addition, the separation of lignin and soluble acids from sugars and reconcentration of sugar and acid solutions should not be forgotten. It should be pointed out here that the separation of soluble sugars and lignin is still challenging and expensive on the industrial scale. The selective acid hydrolysis of hemicelluloses to produce sugars is an interesting process, especially for the production of rare sugars, which are highly value-added compounds in future biorefinery. In addition, acid hydrolysis has been stated to be more efficient than the enzymatic one.¹⁹ Furthermore, in enzymatic hydrolysis of oligomers, the action of several enzymes is needed. The main part of sections 4–7 reviews the acid hydrolysis of hemicelluloses from biomass and gives only some comparisons of cellulose hydrolysis.

One of the best methods to achieve quantitative saccharification of wood is to use a two-step method to saccharify Douglas fir as follows: acid hydrolysis with 72% sulfuric acid at 30 °C for 1 h, followed by a secondary hydrolysis using 4 wt % sulfuric acid at 121 °C for 1 h. In the first step, oligosaccharides were formed, whereas in the second step, monomeric sugars were obtained as products. Alternatively the second hydrolysis was performed with 1 wt % sulfuric acid to produce xylose and arabinose, which are more sensitive to further reactions.²³⁶

Selective dilute acid hydrolysis of hemicelluloses from both wood chips and agricultural wastes has been investigated by

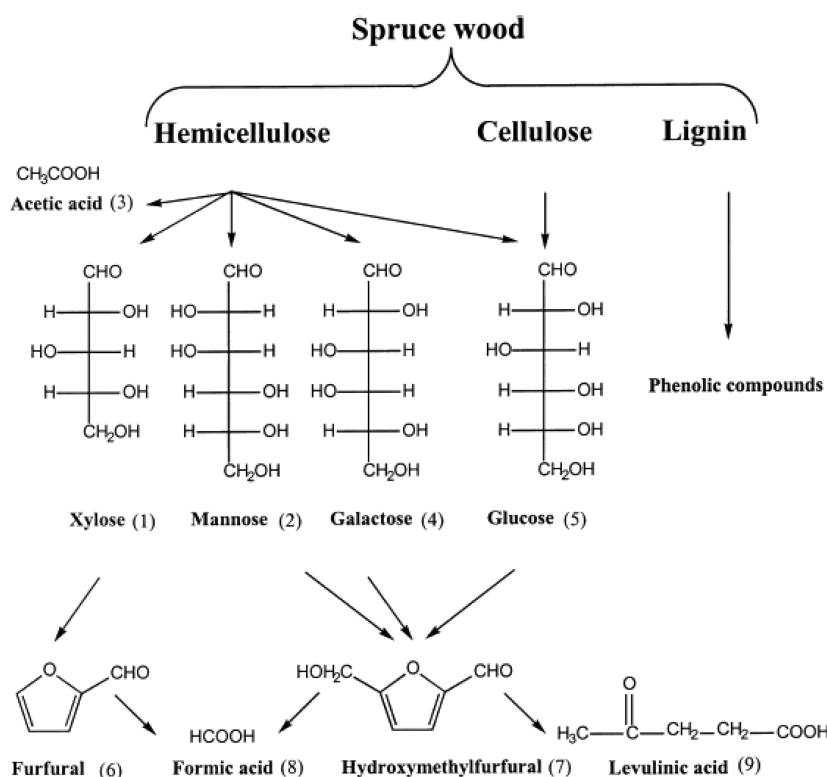


Figure 7. Simplified reaction scheme of acid hydrolysis of lignocellulosic material.⁶⁶ Reprinted with permission from Elsevier.

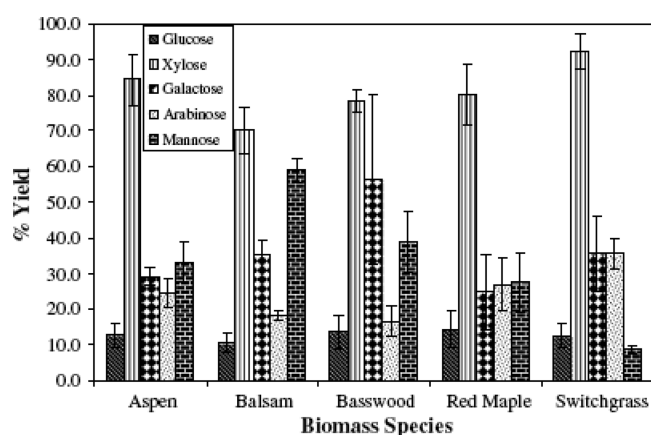


Figure 8. Average sugar yields from eight acid hydrolysis experiments using different wood species as raw material in a temperature range of 160–190 °C. The sulfuric acid concentration varied in these experiments in a range of 0.25–1 wt %.¹¹³ Reprinted with permission from Elsevier.

several groups. Acid hydrolysis of wood chips has been studied for different tree species, such as aspen,^{26,37,71,74} birch,⁷¹ paper birch,^{50,74} willow,⁷¹ pine,^{71,84} spruce,⁷¹ Eucalyptus,⁷³ Loblolly pine,⁶⁰ poplar,⁸⁴ yellow poplar,^{57,104} oak,⁵² Southern red oak,^{74,110} red oak,⁴³ and a mixture of Ponderosa pine and white fir chip,⁸⁷ as well as a mixture of northern hardwood chips from the U.S.A.⁸³ Furthermore, acid hydrolysis of wood residue and hardened saps, such as branches, foliage, and bark of, for example, *Eucalyptus grandis*²⁰ and gum arabic,⁷⁷ has been studied.

Agricultural residues, such as corn stover,^{81,93,97,98} corncobs,²⁵ rice straw,^{85,86,92} rice hull,¹²² switchgrass,^{46,221} corn fiber,¹⁰⁹

envelopes of corn grains,⁷⁶ cashewnut shells,⁸² sugar cane bagasse,^{55,69,72,89,92,108,123,128} sugar beet pulp,^{44,102,107,110,182,186} wheat straw,^{19,52,56,141} maize straw,⁸⁴ tobacco stalk,¹⁴¹ corn stalk,⁹⁴ and sunflower stalk,^{30,49,141} sunflower husk,²⁵ and cotton husk⁴⁸ have been used as raw materials for acid hydrolysis. Furthermore, other spent liquors, such as brewer's spent grain⁶² and green liquor, which is a partially recovered pulping liquor from the kraft process,⁸³ have been used as sugar sources in acid hydrolysis.

In addition to lignocellulosic materials, acid hydrolysis has also been applied for extracted hemicelluloses, such as *O*-acetylgalactoglucomanan,⁸⁰ arabinogalactan,^{78,79} and oligosaccharides^{32,101} (see section 5.7.).

4.1. Effect of Lignocellulosic Material Matrix

As mentioned above, different kinds of raw materials have been used in acid hydrolysis to produce sugars, for example, wood chips from hardwood and softwood as well as agricultural⁸⁴ and hemicellulose fractions.^{79,80} In acid hydrolysis of wood chips, there are variations depending on the tree type; for example, softwoods, especially pine, are generally more difficult to hydrolyze than hardwoods.⁶⁰ When acid hydrolysis of different hardwoods, for example southern red oak, quaking aspen, and paper birch, was compared, it was observed that under similar hydrolysis conditions there were only small differences in the total xylose release with diluted sulfuric acid as catalyst.⁷⁴ One example of the optimum acid hydrolysis conditions for a softwood species, Loblolly pine, is given in ref 60, in which nearly complete selectivity toward the hydrolysis of hemicelluloses can be achieved under mild acid conditions, 150 °C, and pH of 1.65 for 60 min, without significant dissolution of cellulose. A typical simplified reaction scheme of the acid hydrolysis of lignocellulosic material is

Table 2. Xylose Yield in Acid Hydrolysis of Biomass and Hemicellulose

entry	raw material	acid	acid concn	temp (°C)	time (min)	yield (%)	ref
1	wheat straw	TFA	1 M	99	420	80	52
2	wheat straw	TFA	0.1 M	99	1380	70	52
3	wheat straw	HCl	1 wt %	99	120	73	52
4	wheat straw	H ₂ SO ₄	2 wt %	90	720	97	56
5	rice straw	H ₂ SO ₄	n.m. ^a	145	20		86
6	rice straw	H ₂ SO ₄	1 wt %	121	27	77	85
7	corn stover	H ₂ SO ₄	1 wt %	140	40	82	97
8	corn cob corn stover	H ₂ SO ₄	0.68 M	140	50	81	93
9	corn stover	H ₂ SO ₄	1.0 wt %	180	0.67	80	46
10	residue from olive oil production	H ₂ SO ₄	0.25 M	220	80	80	61
11	residue from olive oil production	H ₂ SO ₄	0.125 M	220	140	74	61
12	residue from olive oil production	H ₂ SO ₄	0.05 M	220	240	66	61
13	brewer's spent grain	H ₂ SO ₄	140 mg/g dry material	140	37	94.2	62
14	sugar cane bagasse	H ₂ SO ₄	0.035 M	160	15	88	89
15	sugar cane bagasse	H ₂ SO ₄	100 mg/g dry mat.	140	20	83.3	69
16	sugar cane bagasse	H ₂ SO ₄	4 wt %	120	60	80	72
17	whole tree chips from softwood	H ₂ SO ₄	0.7 wt %	190	3	70.3	88
18	eucalyptus chips	H ₂ SO ₄	0.5 wt %	140	10	21.18 ^b	73
19	southern red oak	H ₂ SO ₄	0.8 wt %	190	0.67	87 ^c	74
20	oak hardwood	H ₂ SO ₄	0.2 wt %	150		83	52
21	aspen wood	H ₂ SO ₄	0.5 wt %	140	16	76.4	26
22	poplar	H ₂ SO ₄	0.9 wt %	180	1	80	46

^a n.m., not mentioned. ^b In g/L. ^c Sum of xylose, xylose oligomers, xylo-uronic acid dimer containing xylose.

shown in Figure 7, in which sugars can react further to primary and secondary decomposition products.

The sugar yields vary much also when the dilute acid hydrolysis of wood chips and agricultural waste is compared. This was the case in the work of Yat et al. (Figure 8);¹¹³ for example, very high mannose yields were achieved from balsam, whereas the yield was very low from switchgrass. Analogously to the work of Yat et al.,¹¹³ the sugar yields were lower for maize straw compared with poplar or pine, due to the fast release from maize and thus further decomposition of the sugars.⁸⁴ In this work, corn straw was hydrolyzed, and the hydrolysis proceeded faster with corn straw than white pine and poplar chips after a two-step pretreatment with dilute sulfuric acid as catalyst. The first step was performed at 180 °C for 30 min, while the second step was carried out at 215 °C for 35 min.⁸⁴

In cellulose dissolution, the challenge is to degrade crystalline domains.³ Thus the dissolution rate of cellulose is leveling off after a certain conversion depending on the crystallinity of cellulose. This degree of polymerization is called leveling-off degree of polymerization.²³⁷ Another challenge in cellulose dissolution with strong acids is the decomposition of the formed sugars.

4.2. Effect of Hemicellulose Structures

The rate of acid hydrolysis of hemicellulose is partially determined by the anhydrosugar structure, for example, whether it is an α - or a β -anomer or it is furanose or pyranose form. It is known that the β -anomers react faster than α -anomers.²³⁸ Furthermore, acid hydrolysis proceeds faster for furanose compared with pyranose, thus indicating that arabinose undergoes easier hydrolysis than xylose.²³⁹ The reason for the faster

furanose hydrolysis rate compared with that of pyranose is the higher structural angle strains in the furanosidic sugar units, whereas pyranose rings are strain-free.

4.3. Acid Hydrolysis of Biomass to Produce Various Rare Sugars

The goal of dilute acid hydrolysis is to selectively remove hemicellulose. The hydrolysis products may contain large oligomers. Typically biomass has been hydrolyzed in a temperature range of 120–220 °C using dilute sulfuric acid as catalyst. Under these conditions, nearly selective hydrolysis of hemicelluloses can be achieved, since only small amounts of glucose have been formed.⁶⁰ Depending on the reaction conditions also other products are formed, for example, oligomers, degradation products of hexoses and pentoses, which are 5-hydroxymethylfurfural and furfural, respectively, and further degradation products (Figure 7).⁶⁰ Undesired products are glucose from dissolution of cellulose, acetic acid, and lignin degradation products, if the aim is to use cellulose as such. On the other hand, cellulose can also be dissolved using harsh conditions, such as presence of concentrated acids (12 M HCl, Bergius process) at room temperature or utilizing diluted acids, for example, at 240 °C, see section 8), if the aim is to maximize the sugar yield.⁶² In this section, the main interest is to report the optimum conditions for acid hydrolysis of biomass to achieve maximum yields of hemicellulose-derived sugars, whereas the effect of temperature, acid strength and type, etc. are discussed in detail in section 5. A special emphasis is put on the relationship between raw material composition and selection of the optimum reaction conditions.

4.3.1. Production of Xylose by Dilute Acid Hydrolysis.

Acid hydrolysis of biomass starting from different raw materials for production of xylose has been intensively studied (Table 2), for

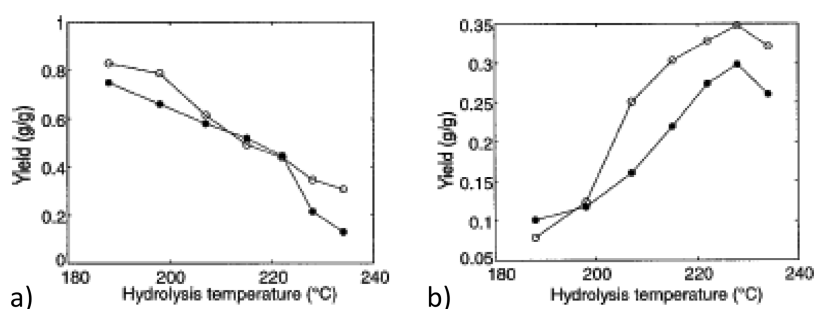


Figure 9. Dilute acid hydrolysis of spruce splinter as a function of temperature: (a) mannose yield per gram mannan; (b) glucose yield per gram glucan. Symbols: the initial solid content of (○) 25 wt %, (●) 33 wt %.⁷¹ Reprinted with permission from American Chemical Society.

example, from sugar cane bagasse,^{69,72,89,121} wheat straw,^{19,52,56,141} rice straw,^{85,86} cotton-seed,⁶⁸ cotton stalk,¹⁴¹ sunflower stalk,^{30,141} corn stover,^{46,97,98} tobacco stalk,¹⁴¹ brewer's spent grain,⁶² green liquor prepulping extract of Northern hardwoods,⁸³ *Eucalyptus grandis* chips,⁷³ poplar,⁴⁶ paper birch,⁵⁰ and aspen hemicelluloses.^{26,59} There is according to our knowledge only one review describing different methods, such as acid hydrolysis, enzymatic hydrolysis, hot water extraction, and microwave treatment, to prepare xylo-oligosaccharides.¹¹⁸

Acid hydrolysis of sugar cane bagasse to produce xylose using sulfuric acid as catalyst has been intensively investigated.^{69,72,89,108} The maximum xylose yields varied in a range of 70–88%, being inversely proportional to temperature and the acid concentration to maximize the xylose yield (Table 2, entries 14–16). Furthermore, about 5% of cellulose was dissolved and only 1.4% of xylose reacted further to furfural indicating that relatively high selectivity toward xylan dissolution was achieved under 160 °C using 0.035 mol/L sulfuric acid as a catalyst despite the fact that the sugar cane bagasse contained originally large amounts of cellulose, about 40 wt %.⁸⁹ About 20% of lignin was dissolved and formed acid-soluble lignin when the dissolution of bagasse was performed with 1 wt % sulfuric acid at 120 °C.⁷² It should be pointed out here that dilute acid hydrolysis of sugar cane bagasse has a potential for producing monomeric sugars, since the solid residue mainly contains cellulose and lignin.⁸⁹

Hemicelluloses for wheat straw, which contains relatively low amounts of cellulose and lignin, were efficiently hydrolyzed with either dilute trifluoroacetic acid (TFA)⁵² or sulfuric acid.⁵⁶ In the former case, the hydrolysis of wheat straw with 1 M TFA at 100 °C gave 23% yield of xylose in 23 h.⁵² This value corresponded to 80% based on the total xylan content. Furthermore, xylose decomposition was minimal under these conditions, but about 10% of lignin was present as water-soluble lignin fragments in the hydrolysate. The benefit of using trifluoroacetic acid as catalyst is that it can be easily separated by evaporation. Mainly xylose and arabinose were obtained as products also during the hydrolysis of wheat straw with sulfuric acid at 90 °C.⁵⁶ Since arabinoxylan contains the arabinose groups in the side chain (see section 2.2), arabinose release is initially faster than that of xylose. It was stated that practically full conversion (about 97%) was achieved in wheat straw hydrolysis during 12 h using 2 wt % sulfuric acid as catalyst giving only traces of glucose,⁵⁶ whereas at low acid concentrations, for example, 0.5 or 1.0 wt % sulfuric acid as a catalyst, the conversions were 36% and 58%, respectively. Analogously to hydrolysis of wheat straw with sulfuric acid,²⁹ also rice straw has been hydrolyzed with this acid.^{85,86}

Acid hydrolysis of corn stover to produce xylose was performed by using sulfuric acid in a temperature range of 140–200 °C.⁹⁷

The highest yield of monomeric xylose, 31%, was achieved at 160 °C after 20 min hydrolysis at pH of 1.62,⁹⁸ whereas only 0.9% of dissolved xylan was in oligomer form. At the same time, the glucose yield was 3.9%, indicating that relatively selective hydrolysis of xylans was achieved. More oligomers were formed under more diluted acid concentrations, at pH of 2.36 during 40 min reaction time. The ratio between xylose and xylooligomers to cellulose was under optimized reaction conditions, at pH of 1.62 and at 160 °C about 8.2 indicating that cellulose dissolution was relatively minor. Also corncob was used as a raw material for hemicelluloses.¹¹⁵ The hydrolysis of xylan from cotton-seed with dilute sulfuric acid at 90 °C was also demonstrated in ref 68. Xylose and xylo-oligomers, which were separated with gel-permeation chromatography, were obtained as main products.

Acid hydrolysis of Brewer's spent grain to produce xylose was investigated with sulfuric acid. This raw material contains about 28% hemicelluloses, 17% cellulose, and 28% lignin. Complete recovery of arabinose and about 94% recovery of xylan could be achieved via acid hydrolysis of brewer's spent grain with diluted sulfuric acid at 120 °C.⁶² Glucose release in this case can be derived both from cellulose and hemicellulose, but it was stated that cellulose is not hydrolyzed under these conditions, at 140 °C using 100–140 mg of sulfuric acid per gram of solid.⁶² Due to the structure of the hemicelluloses, such as arabinoxylan present in brewer's spent grain, the arabinose release was faster than that of xylose (see section 5.4.4.). The amount of lignin decomposition products was correlated with the acid concentration (see section 5.4.4) and the liquid-to-solid ratio (see section 5.5).

The green liquor extract containing oligomeric hemicelluloses was hydrolyzed by dilute sulfuric acid in a temperature range of 100 to 160 °C.⁸³ This raw material contained 9.5 g/L xylan, 0.6 g/L glucan, and 1.7 g/L arabinan, and their ratio corresponds to the ratio of hemicelluloses found in arabinoglucuronoxylan from northeast hardwood chips in the U.S.A. The optimum temperature for hydrolysis was 140 °C, giving a sugar yield of 91%. The furfural amounts increased up to 3.4 times when the temperature increased from 140 to 160 °C due to the dehydration of xylose (see section 5.6). The amount of acetic acid formed by deacetylation exhibited a maximum between 130 and 140 °C.

Xylose has been produced via acid hydrolysis of wood chips, such as *Eucalyptus grandis* chips,⁷³ aspen,^{26,59} paper birch,⁵⁰ and poplar.⁴⁶ Typically slightly higher temperatures have been used for wood chips compared with sugar cane bagasse (Table 2, compare entries 17–22 with entries 14–16). This might be due to the lower cellulose content in bagasse (about 40%) compared with wood.¹⁸⁰ Especially, poplar contains about 44% cellulose.¹⁹² Xylose yields varied in a range of 70–87% depending on the

reaction conditions. Xylose was found in hydrolysates as monomers, as oligomers, and as xylose—uronic acid dimers, when the raw material is hardwood. Under optimized conditions, at 190 °C using 0.8 wt % sulfuric acid as a catalyst, 75% of the xylose was present as monomer in the acid hydrolysis of southern red oak, whereas only 8% was present as oligomers and 4% as xylose—uronic acid dimers. Furthermore, 7% of the total xylose was in the residue, and only 6% was degraded.⁷⁴ The acetyl removal was slightly faster than xylan removal at lower temperatures during acid hydrolysis of paper birch with sulfuric acid as a catalyst, whereas at higher temperatures a linear dependency between acetyl and xylan removal was observed.⁵⁰ These results with different temperatures suggest that at lower temperatures, both direct hydrolysis of acetyl groups and hydrolysis from xylans take place.

Acid hydrolysis of xylans has been investigated also with model compounds, such as xylobiose using dilute sulfuric acid as catalyst.⁹⁸ In their work, an optimum pH of 2–3 was found to achieve maximum xylose yield (see section 5.7).

4.3.2. Acid Hydrolysis To Produce Mannose. Acid hydrolysis for production of mannose has been scarcely investigated,^{71,80} even though mannose has high potential in further applications (see section 3.1.2). The starting material for mannose has been either wood chips⁷¹ or *O*-acetylgalactoglucmannan separated from TMP-waste waters.⁸⁰

A combined steam-diluted acid treatment was applied for releasing sugars from spruce. In this method, spruce splinter was hydrolyzed in 5 g/L sulfuric acid in the temperature range 188–234 °C as follows: steam was added to the mixture of wood splinter—dilute sulfuric acid, and the mixture was heated up to the desired temperature and kept at this temperature for 7 min. Thereafter, the vessel was decompressed and discharged. The dissolved mannose and glucose concentrations were determined at different temperatures. The mannose yield was the highest: about 82 g/g calculated based on the mannan (Figure 9a).⁷¹ With increasing temperature, however, the mannose yield decreased from 82 g/g to the level of 0.1 g/g at 234 °C. At high temperatures, mannose is dehydrated to 5-hydroxymethylfurfural, the kinetics of which is discussed in more detail in section 5.6. The selectivity of mannose dissolution decreased strongly when the temperature was increased due to the dissolution of cellulose and formation of glucose (Figure 9b) (see section 5.2).

Acid hydrolysis of *O*-acetylgalactoglucmannan was studied using HCl as catalyst in the temperature and pH ranges of 50–90 °C and 1–3, respectively.¹⁴² The raw material contained 66% of mannose, 17% of glucose, and 11% of galactose. In their work,¹⁴² mainly the reaction kinetics was investigated, and no separate monomer analyses were performed. Instead, the molar mass and the molar mass distribution were determined by high-pressure size-exclusion chromatography in combination with a multiangle laser light scattering instrument. The maximum yield of mannose was thus not reported, but high monomer yields, about 580 mg/g of the polymer, were achieved in the hydrolysis at 90 °C at pH 1 after 2800 min. The kinetic data, mechanism and modeling of the acid hydrolysis of *O*-acetylgalactoglucmannan are reported in sections 5, 6 and 7.3. It should be pointed out that the mannose yield after the hydrolysis could be increased by enzymatically converting glucose to mannose, since mannose is a valuable rare sugar.²¹²

4.3.3. Acid Hydrolysis of Biomass To Produce Galactose. There are only a few reports of the acid hydrolysis to

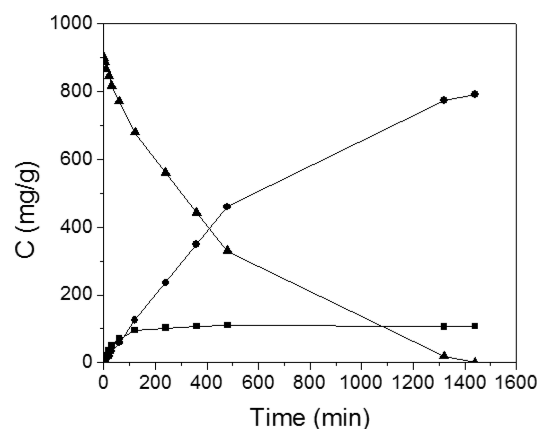


Figure 10. Formation of arabinose and galactose in acid hydrolysis of arabinogalactan at 90 °C and pH 1 using HCl as a catalyst, adapted from ref 74. Symbols: (▲) arabinogalactan; (●) galactose; (■) arabinose.

produce galactose starting either from arabinogalactan or from industrial waste of cashewnut shells.^{78,79,82} Very high yields of galactose, about 97.5–99%, were achieved when the acid hydrolysis of galactoarabinan was performed at 100 °C for 24 h using HCl as a catalyst.⁷⁸ It should, however, be stated that the raw material, galactoarabinan, contained maximally 1.5% arabinose and up to 1 wt % galacturonic acid. When acid hydrolysis of arabinogalactans containing galactose and arabinose in a molar ratio of 6:1 was performed, the maximum concentration of galactose was achieved in 1440 min using pH of 1 at 90 °C⁷⁹ (Figure 10). The arabinose release was much faster than that of galactose, being complete after 160 min. The effect of temperature and pH was also studied and is reported in section 5.

The maximum galactose yield from cashewnuts shells was 3.2 wt % after 12 h acid hydrolysis at 100 °C using 1 M sulfuric acid as a catalyst.⁸² This corresponds to 32 g of galactose of high purity per 1 kg of cashewnut shells, which is an industrial waste. In their work, a process scheme was proposed that included neutralization after hydrolysis with barium sulfate. Thereafter the hydrolysate was concentrated and decolorized, and galactose was crystallized, dried, and made to powder.

4.3.4. Acid Hydrolysis of Biomass To Produce Arabinose. Arabinose can be selectively produced via acid hydrolysis of arabinan in sugar beet pulp^{102,170} or in envelopes of corn grains using diluted oxalic acid or hydrochloric acid as catalysts.⁷⁶ In the selective acid hydrolysis, the key issue is the acid concentration; for example, with dilute acids, a more selective hydrolysis of arabinose has been achieved compared with the case of stronger acids. The maximum yield of L-arabinose was about 16% from the theoretical value obtained with 0.022 M oxalic acid at 130 °C. Under these conditions, there were, however, also 36.4% xylo-oligosaccharides and 4.4% xylose.⁷⁶ In the process description, it was proposed that the hydrolysate should be filtered and neutralized. Xylooligosaccharides could be separated with membrane filtration, gel filtration, or chromatographic separation. The effect of the acid concentration on the selectivity is discussed in more detail in section 5.4.

In the acid hydrolysis of arabinogalactans, the arabinose hydrolysis at pH 1 at 90 °C using hydrochloric acid as a catalyst was complete already after 120 min (Figure 10), whereas galactose was continuously produced via backbone cleavage (see section 4.3.3).⁷⁹ Furthermore, the rate constant for the

release of arabinose was 0.7-fold larger than that of galactose. Analogous results have been obtained from acid hydrolysis of arabinoxylans starting from wheat, rye, barley, and rice.²⁷⁰ The reason for the fast release of arabinose is its location in the side chain of the galactose backbone (see section 5.4.4).

Arabinose was also produced via acid hydrolysis of corn stover by using acetic acid as a catalyst at 195 °C.⁸¹ The maximum arabinose yield was 25% from corn stover with 0.2 g of acetic acid per gram of corn stover. Under these conditions, about 3% of arabinose existed in oligomeric form.⁷⁶ Furthermore, almost no arabinan was left in the water-insoluble residue after this treatment, thus suggesting that this method is efficient for producing arabinose from corn stover. Arabinose was not, however, very stable at this temperature, for example, when 1 wt % acetic acid was used as a catalyst, almost half of the arabinose was degraded⁷⁶ indicating that the hydrolysis temperature was too high. Additionally, arabinose was obtained via acid hydrolysis of sugar beet pulp with acetic acid as a catalyst, but this time at a much lower temperature than in the work of ref 142, namely, at pH 0.8 at 90 °C.¹⁰⁷ The filtrate was thereafter neutralized to pH 6 and filtered. Arabinose was recovered via chromatographic separation with the yield of 15 wt % of the pulp dry weight.¹⁰⁷

4.3.5. Acid Hydrolysis of Biomass To Produce Rhamnose. Selective acid hydrolysis of gum arabic (see section 2.2) for production of rhamnose was reported in ref 77. When dilute HCl was used as catalyst, selective rhamnose hydrolysis was achieved using hydrolysis at 100 °C for 2 h using 0.3 M HCl as a catalyst. The liquid phase was neutralized and evaporated. The undissolved solid was hydrolyzed in the second batch, and thereafter the two hydrolysates were combined, and acetonitrile was used as an antisolvent to precipitate sugars. The precipitated sugars were dissolved in a small amount of water and separated chromatographically. Finally 99.5% pure rhamnose was achieved in a yield of 84%. Analogous results were achieved using 0.2 M H₂SO₄ as a catalyst. When, however, the acid concentration was increased to 1–2 M HCl or 1.5 M H₂SO₄, the selectivity for rhamnose hydrolysis decreased very much and the purification process became economically inefficient (see section 5.4.4).

5. KINETICS OF ACID HYDROLYSIS: COMPARISON BETWEEN SELECTIVE DISSOLUTION OF HEMICELLULOSES AND ACID HYDROLYSIS OF CELLULOSE

In order to determine the kinetics of acid hydrolysis of lignocellulosic material accurately, it is important to perform the analysis of oligomers, sugars (monomers, dimers), and their degradation products.⁵² In addition, also the kinetics of lignin dissolution and formation of acetic acid can be interesting to get an overall picture of the acid hydrolysis process. Analysis of oligomers is possible for molecules exhibiting up to seven monomer units,⁵¹ although even more than seven cellodextrins have been detected.^{235,240} In several publications, oligomer analysis^{51,56,81,84,93} or average molecular weight of the polymer as a function of time^{79,80} have been presented. However, in the majority of publications, no data about oligomer concentrations have been published.^{73,85,86} There are several parameters that should be optimized to maximize the yields of sugars originated from hemicelluloses, such as chip size, temperature, acid type, acid concentration, and solid concentration. In addition sugar decomposition kinetics is reviewed below. The comparison of different kinetic data from acid hydrolysis of hemicelluloses is difficult as also stated earlier, since hydrolysis kinetics is dependent on

substrate species and reaction conditions.²⁶ The kinetics of cellulose dissolution is also shortly reviewed here in order to elucidate the difference in the optimum reaction conditions used for hydrolysis of hemicelluloses and cellulose. Different optimum reaction conditions are used for hydrolysis of hemicelluloses and cellulose. Different optimum reaction conditions are related to the structural differences between hemicelluloses and cellulose. Cellulose required “inhomogeneity of substrate” in kinetics,^{241–243} and in hydrolysis of hemicelluloses, this approach is even more natural. Up to now, there are very few papers that treat hydrolysis of hemicelluloses in a quantitative manner.⁸⁰

5.1. Wood Chip and Particle Size

Chip size has been reported to have a minor effect on the acid hydrolysis of hardwood with dilute sulfuric acid for a high liquid-to-wood ratio,⁷⁴ but on the other hand, when less liquid is used the fraction of the xylan remaining in the residue is increased. This fact is not very encouraging when considering the economical feasibility of the industrial application. The particle size did not have any significant effect on the hydrolysis rate in a fraction of 10–30 mesh in the acid hydrolysis of aspen, balsam fir, basswood, and red maple using sulfuric acid as a catalyst.¹¹³ On the other hand, large chip thicknesses retarded the acid hydrolysis of aspen wood, and xylose yields decreased.²⁶ The reason for this is the transient temperature effect, which affects xylose yield. In ref 26, the chip thickness was varied in a range of 0.1–1 cm and hydrolysis was performed at 140 °C. Furthermore, kinetic models were developed in ref 26 that included transient temperature effects as a function of chip sizes.

5.2. Effect of Temperature

The temperature is one of the most crucial parameters in dilute acid hydrolysis of lignocellulosic materials and hemicelluloses, since it affects the hydrolysis rate and selectivity. Temperature effects have thus been extensively investigated in selective acid hydrolysis of hemicelluloses.^{20,23,26,30,44,46,50,60,69,72–74,76,79,80,83,89,91,95,97,98,106,127}

It is known that under moderate temperatures, in the range of 140–190 °C, most of the hemicelluloses are recovered as dissolved sugars. Both optimum temperatures for acid hydrolysis of lignocellulosic materials and apparent activation energies are reviewed below, whereas the dissociation of acids at high temperatures and sugar decomposition kinetics are reported in sections 5.4.2 and 5.6, respectively.

5.2.1. The Effect of Hydrolysis Temperature. There are several studies in which an optimum reaction temperature has been determined experimentally for the acid hydrolysis of biomass. It should, however, be pointed out that the optimum reaction conditions are selected from several interrelated parameters, such as time, acid concentration, type of biomass, and its concentration, which makes the comparison of different parameters difficult.

Typically in selective biomass hydrolysis for the production of xylose from xylan, a maximum yield of xylose was achieved at optimum temperature and time.^{69,72,74,91,117} The optimum yield was, however, dependent not only on the temperature but also on the acid concentration,^{72,74} as well as on the initial biomass concentration.⁶⁹

The optimum hydrolysis temperatures are also dependent on the raw materials and mainly on their cellulose and lignin contents (see section 2.2). In wheat straw, the hydrolysis between 30 and 90 °C using 2.0 wt % sulfuric acid as a catalyst⁵⁶ resulted in nearly complete conversion of hemicelluloses at 90 °C, whereas at 34 °C, no reaction occurred. There are

Table 3. Apparent Activation Energies for Acid Hydrolysis of Different Hemicelluloses

entry	raw material	temp range (°C)	acid concn	apparent activation energy (kJ/mol)	ref
1	arabinogalactan	80–100	1 M HCl, pH 1	126, ^a 135 ^b	79
2	inulin	7–100	pH 2–4.2 ^c	109	95
3	O-acetylglactoglucomannan	50–90	1 M HCl, pH 1–2	150	80
4	sugar cane bagasse	100–128	2–6 wt % H ₂ SO ₄	109	91
5		120–160	1–4 wt % H ₂ SO ₄	82.8 ^d	72
6	birch	100–130	0.04–0.09 M H ₂ SO ₄	127, ^d 156 ^e	50
7	aspen	95–160	dilute H ₂ SO ₄	117, ^d 155 ^e	59
8	poplar	160–189	0.6–1.2 wt % H ₂ SO ₄	176, ^d 192 ^e	46
		140–160	0.49 wt % H ₂ SO ₄	117 ^d	117
9	corn stover	160–189	0.6–1.2 wt % H ₂ SO ₄	130, ^d 168 ^e	46
10	wheat straw	95–160	0.5 wt % H ₂ SO ₄	50, ^d 105 ^e	59
11	switchgrass	160–189	0.6–1.2 wt % H ₂ SO ₄	169	46
12	corn cobs, corn stover	140–170	0.47–1.95 wt % H ₂ SO ₄	148, ^d 199 ^e	93
13	sunflower residue	110–140	0.5–6 wt % HCl	101.2	30
		110–140	2–8 wt % H ₂ SO ₄	101.3	30

^a Arabinose. ^b Galactose. ^c Different acids: sulfuric, hydrochloric, and acetic acid. ^d Fast-reacting xylan. ^e Slow-reacting xylan.

also other publications reporting relatively low optimum temperatures for maximizing the yield of xylose from straw materials (Table 2).^{52,56}

In hydrolysis of wood chips, usually higher optimum temperatures are required compared with those for straw. A higher mannose yield can be achieved in acid hydrolysis of spruce at low temperatures, about 180 °C compared with the case at 230 °C.⁷¹ On the other hand, the glucose yield was the highest at the highest investigated temperature, at 230 °C, since it is thermodynamically more stable than xylose. This result can be partially explained by the fact that different sugar units have different rates for acid hydrolysis. Glucosides are hydrolyzed more slowly compared with mannosides (see section 5.7).²²⁸ Furthermore, xylose yields from birch also decreased about 90% from 0.7 g/g hydrolysate to about 0.07 g/g hydrolysate, when the hydrolysis temperature increased from 188 to 230 °C.⁷¹ This can be explained by further dehydration reactions of xylose (see section 5.6).

If the aim is to hydrolyze cellulose, it can be hydrolyzed either with concentrated mineral acids already at room temperature⁶³ or alternatively at a temperature range of 190–240 °C with diluted sulfuric acid.^{105,132,139} According to ref 63, the former process, performed with 40 wt % HCl at room temperature, suffers from low selectivity, since large amounts of 5-hydroxymethylfurfural and levulinic acid are formed. The latter one can be performed in a plug flow reactor with a short residence time, 0.22 min, in order to achieve high yields of glucose, about 50% using 1 wt % sulfuric acid at 240 °C.¹⁰⁵ Furthermore, the maximum yields of glucose achieved in a batch reactor with 0.07 wt % H₂SO₄ were 62% in 30 min and 59% in 25 min, respectively.²⁴⁴ Nonconventional heating, such as microwave, was shown to increase sugar yields in cellulose dissolution with 20 wt % HCl as a catalyst compared with conventional heating.¹²⁹

Additionally, a percolating reactor has been applied for dissolution of cellulose¹³² and an optimum glucose yield being 71% of the theoretical maximum was achieved at 215 °C under 34.5 MPa by using 0.05% sulfuric acid as a catalyst. The hydrolysis rate of cellulose was very slow below 212 °C, whereas above this temperature, the rate was enhanced very much. This discontinuity in

the hydrolysis rate was explained by physical changes in the solid material at this temperature. Above 220 °C, a lower glucose yield was achieved due to glucose decomposition.

5.2.2. Apparent Activation Energies. The apparent activation energies have been determined for the selective acid hydrolysis of wood chips,^{46,50,59} for agricultural wastes,^{46,59,72,91,93} and for isolated hemicelluloses.^{79,80,95,127} Typically for wood chips, there are slight differences in the apparent activation energy, for example, high apparent activation energies have been determined for poplar,⁴⁶ whereas lower ones are obtained for some other hardwood species (Table 3).^{50,59}

Apparent activation energies for acid hydrolysis of isolated hemicelluloses, such as arabinogalactan and O-acetylglactoglucomannans are reported in Table 3, entries 1 and 3.^{79,238} In acid hydrolysis of arabinogalactan, lower apparent activation energy was achieved for arabinose compared with galactose, as expected, since arabinose is in the side chain of the galactan backbone. This also follows the trend of hydrolyzing methyl glycosides (see section 5.7). For another hemicellulose, O-acetylglactoglucomannans, which were hydrolyzed by using HCl as a catalyst at 50–90 °C, an apparent activation energy of 150 kJ/mol was reported.¹⁴² The higher apparent activation energy reported for the hydrolysis of O-acetylglactoglucomannan compared with arabinogalactan can be partially explained by the nature of the ether linkage and sugar structure. It is known from model compound studies that glucosides and mannosides are harder to hydrolyze than galactosides (see section 5.7).²³⁸

In acid hydrolysis of sugar cane bagasse, the apparent activation energy for the xylan hydrolysis was 82.8 kJ/mol in a temperature range of 120–160 °C, whereas about 36 kJ/mol higher apparent activation energy was reported for xylose decomposition compared with xylan hydrolysis.⁷² In some works,^{46,50,60,111} the fraction of slow- and fast-reacting xylan was determined, being for the former typically in a range of 0.2–0.32.⁵⁰ The fast-reacting xylan exhibited about 8–23% lower apparent activation energy compared with slow-reacting xylan (see Table 3, entries 8–12, 14, 15).

Apparent activation energies have also been determined for the decomposition of sugars.⁷² In the acid hydrolysis of sugar cane

Table 4. pK_a Values of Different Acids at 25 °C¹⁸⁵

acid	pK_a
hydrochloric acid	−6
sulfuric acid	−3
nitric acid	−1.32
trifluoroacetic acid	0.23
oxalic acid	1.23 ²⁶⁹
maleic acid	1.9 ¹³³
phosphoric acid	1.96
formic acid	3.7
acetic acid	4.8

bagasse with hydrochloric acid, the apparent activation energy for the arabinose decomposition was only 29% of the value achieved for xylose formation.⁷² On the other hand, the arabinose decomposition was faster than that of xylose using phosphoric acid as a catalyst indicating that there might be several interrelated factors determining the kinetics of sugar decomposition.⁵⁵

Apparent activation energies for the dissolution of cellulose have varied in a range from 118 kJ/mol²³⁹ to 179 kJ/mol.¹⁰⁰ These variations can partly originate from the variations of diffusion in the early state of the hydrolysis. In dilute acid hydrolysis of α -cellulose using 0.07% sulfuric acid as a catalyst in a temperature range of 185–245 °C in a batch reactor, Arrhenius' equation was applied for the experimental data. An interesting increase in the reaction rate was observed in the temperature range of 215–245 °C compared with the case in a low temperature range of 185–205 °C.¹³⁸ This result was explained by the change in the physical state of cellulose. Above 215 °C, the physical factor retarding the cellulose hydrolysis is eliminated.

5.3. Effect of Acid Type

5.3.1. Homogeneous Acid Catalysts. Several inorganic and organic acids have been used as catalysts in the hydrolysis of lignocellulosic material and hemicelluloses, such as sulfuric acid,^{19,20,29,30,32,34,37,39,42,43,47,50,51,53,56–58,60,62,68–74,76,77,83–89,95–98,102,104,107,108,112,113,122,127,131,189} phosphoric acid,^{55,60} acetic acid,^{95,107} oxalic acid,^{76,120} trifluoroacetic acid,^{52,60} and maleic acid,¹³³ as well as mixed acids, such as HCl and H₂SO₄, H₂SO₄ and H₃PO₄, etc. The pK_a values of different acids used in the acid hydrolysis of hemicelluloses are shown in Table 4.

Organic acids have some beneficial properties in acid hydrolysis, since they are mild acids and can thus promote selective acid hydrolysis of hemicelluloses.⁵² One example of that is the use of oxalic acid for selective removal of arabinose from arabinoxylan.²¹ Furthermore, trifluoroacetic acid can be evaporated from the reaction mixture;⁵² thus the neutralization step, which causes salt formation, is omitted. Carbonic acid, which was formed in contact with water at 80 °C and 3.4 bar, was able to extract hemicelluloses from rice straw.¹³⁰ Thereafter, in the second step, the cellulose was hydrolyzed at 100 °C under 1.4 bar with carbonated water. As a result about 41% of cellulose was hydrolyzed. Furthermore, maleic acid was more selective than sulfuric acid in acid hydrolysis of cellulose, since it did not catalyze degradation of glucose.¹³³ Cellulose hydrolysis selectivity was also improved by adding a small amount of acetic acid into the reactor containing hot water at 260 °C.¹³⁴

Among inorganic acids, sulfuric acid is an inexpensive acid,²⁴⁵ being able to release up to 90% hemicelluloses from biomass, but

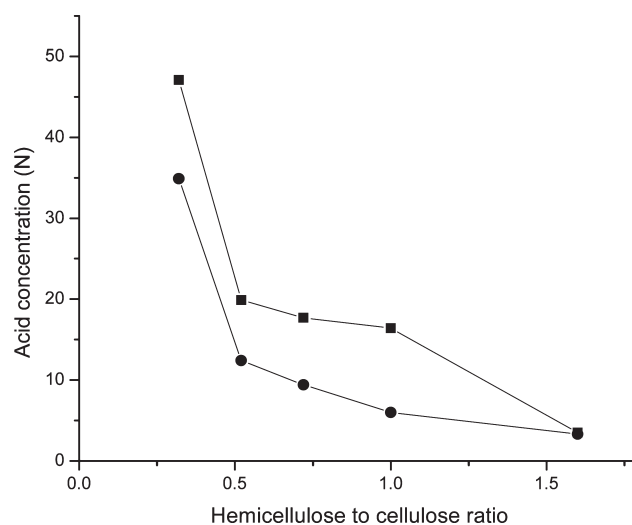


Figure 11. Ratio between dissolved hemicellulose and cellulose in acid hydrolysis of sugar beet pulp at 80 °C using (◆) HCl and (■) H₂SO₄ as a catalyst. Reproduced based on data in ref 44.

on the other hand there are high material costs, especially if high pressures are needed. Furthermore, the neutralization step creates a solid waste, such as gypsum.¹¹⁰ Special care should be taken when working with nitric acid, since this acid can create gaseous nitric oxides around 200 °C, and thus its use should be avoided at high temperatures.⁶⁰ Dilute sulfuric acid¹⁰⁸ and hydrochloric acid are very corrosive⁶⁰ compared with others such as phosphoric acid. Furthermore, it was pointed out that despite use of dilute acids, the materials of construction and high pressures make the process expensive.²⁴⁵ Heterogeneous acids could facilitate easy catalyst separation and reuse. Some heterogeneous catalysts have been applied for acid hydrolysis of biomass (see section 5.3.2).

5.3.1.1. Effect of Acid Type on Hydrolysis Rate. The rate of the acid hydrolysis has been reported to be acid independent in the case of hydrolyzing inulin.⁹⁵ The reaction order with respect to the acid is reviewed in section 5.4.3. However, differences in the performance of different acids have been observed on the dissolution power of glucan,⁴⁴ decomposition of xylose,⁵² etc. (see section 5.4.4).

5.3.1.2. Effect of Acid Type on Hydrolysis Selectivity. The acid hydrolysis selectivity is affected by the acid type, which in turn enhances either sugar decomposition or cellulose dissolution in different ways.

Nitric acid is known to enhance the degradation of pentoses and thus catalyze furfural formation.⁶⁰ The decomposition kinetics of xylose was faster in HCl compared with trifluoroacetic acid⁵² when 1 M acid was used in acid hydrolysis of wheat straw to achieve xylose. On the other hand, xylose decomposed faster in sulfuric acid than in HCl.⁷² These results indicate that the selectivity of the process is decreased. It was also found that higher sugar yields were achieved during sunflower residue hydrolysis at 120 °C when using HCl as a catalyst compared with H₂SO₄.³⁰ In this case, however, the total sugar content was analyzed by titration, and thus this value contained also dissolved glucans. Trifluoroacetic acid caused less decomposition of monosaccharides compared with sulfuric acid.^{60,246} Furthermore, sugar decomposition has been suppressed by addition of protectors, such as ethyl–ethyl ketone in the hydrolysis mixture.

As a result, higher yields of monosaccharides were reported compared with the case without protectors.¹²³

The acid type and concentration affect also hydrolysis selectivity, especially for cellulose dissociation. With HCl more glucan was dissolved compared with the case of sulfuric acid.⁵² Analogously sulfuric acid was more selective than HCl to dissolve hemicelluloses than cellulose from sugar beet pulp at 80 °C, at a given solid to liquid ratio (Figure 11).⁴⁴ The ratio between the dissolved hemicelluloses to cellulose decreased, however, with increasing the initial acid concentration.⁴⁴ The desired level of hydrolyzed cellulose should be below 5%. Moreover, sulfuric acid was more selective in hydrolyzing hemicelluloses compared with the case with HCl.⁴⁴ When acid hydrolysis of sugar beet pulp was performed at 80 °C for 2 h with either 0.16 M H₂SO₄ or HCl, the hemicelluloses-to-cellulose ratio was 47.1 for the former one, whereas it was 34.9 for the latter acid.⁴⁴

5.3.2. Heterogeneous Acid Catalysts. The benefit of using heterogeneous catalysts is their easy separation, which implies that the neutralization step of the hydrolysate can be avoided. During the neutralization step, salts are formed, which in turn should be removed via filtration.⁵⁵

There are only very few reports of using solid catalysts for hydrolyzing hemicelluloses.²³ Inulin has been hydrolyzed to fructose over a zeolite at 100 °C. The conversion of inulin was 95% within 2 h, and no 5-hydroxymethylfurfural was formed. Furthermore, repeated experiments of hydrolyzing inulin over zeolite showed no decrease of the catalyst activity. Between the experiments, zeolite was washed with deionized water and dried prior to the forthcoming experiment.²³

Cellulose hydrolysis has also been investigated over heterogeneous catalysts in the presence of hydrogen at 190 °C.²⁴⁷ The yield of glucose was, however, in most cases very low, below 4%, and thus it was concluded that metal has beneficial effect on cellulose dissolution. The most active material for the acid-catalyzed hydrolysis of cellulose was HZSM-5 giving about 3.4% yield of glucose.²⁴⁷ Additionally, crystalline cellulose (crystallinity of 80%) was hydrolyzed at 100 °C in water using solid sulfonated carbon material as a catalyst.¹³⁶ The main products were 1,4-glucan and glucose totaling about 68% yield after 3 h reaction time. A cluster heteropolyacid catalyst in a pseudomolten state, 40–50 °C, was used to dissolve cellulose in aqueous mixture. In the second step, saccharides together with undissolved material were precipitated by addition of ethanol.¹³⁷

5.4. Effect of Acid Concentration on Hydrolysis

The effect of acid concentration has been investigated in several studies.^{19,20,32,44,56,62,69,72–74,76,77,79–81,83,85,87,89,91,95,98,106,109}

Generally, it is accepted, that the acid hydrolysis rate is increased with increasing acid concentration.²⁴⁸ Substrate homogeneity or heterogeneity plays a crucial role in hydrolysis kinetics, which has been clearly shown in development of kinetic models. For example, when a lignocellulosic material is semicrystalline containing amorphous and crystalline fractions, such as cellulose,⁵ more complicated kinetic models should be applied for description of the hydrolysis kinetics (see section 7).^{241,242} This heterogeneity has also been taken into account when studying the dissolution with diluted acids, which proceeds via fast and slow reacting fractions,⁴⁶ whereas if the acid concentration is very high, a homogeneous solution of wood chips is achieved in concentrated acid solutions, as was the case of 33% sulfuric acid used in dissolution of hardwood and softwood chips at 100 °C.¹²⁶ A high acid concentration is

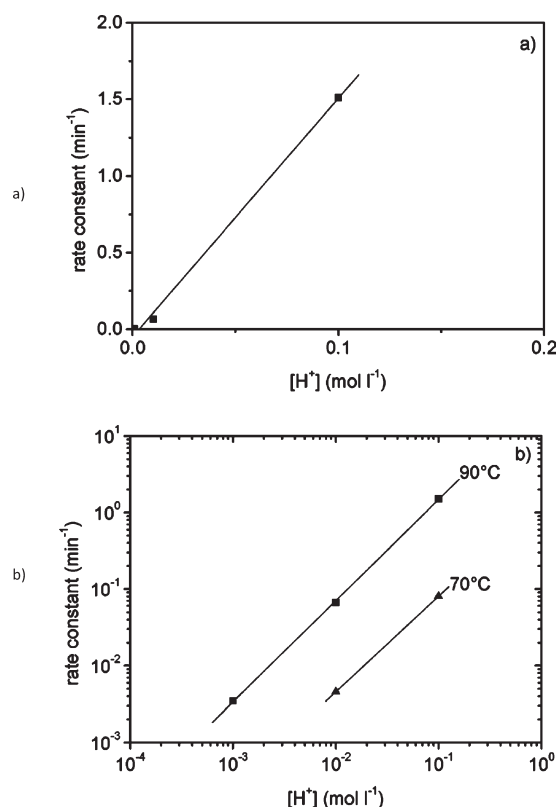


Figure 12. (a) Rate constants of acid hydrolysis of O-acetylglactoglucan as a function of H⁺ concentration at 90 °C and (b) double logarithmic rate constant versus H⁺ concentration of the acid hydrolysis of O-acetylglactoglucan at 70 and 90 °C.¹⁴² Reprinted with permission from American Chemical Society.

not, however, only beneficial, since at too high acid concentrations, the selective acid hydrolysis of hemicelluloses is not possible, because side reactions and glucan hydrolysis occur. The acid concentration is affected by the neutralization capacity of the biomass, as well as the pretreatment temperature, since the dissociation of sulfuric acid is limited at high temperatures. If in the dilute acid hydrolysis pH is about 1.9, it corresponds to the pK_a value of the bisulfate ion when sulfuric acid is used as a catalyst.⁷² Thus in this case, it was assumed that sulfuric acid was active as a monoprotic acid. The decomposition of sugars to 5-hydroxymethylfurfural and furfural is enhanced with increased acid concentration.⁸⁵ Especially at high temperatures, about 180 °C, the xylose yield from acid hydrolysis of corn stover was affected by the acid concentration; the higher the acid concentration the lower the xylose yield.⁴⁶ Furthermore, more cellulose is hydrolyzed with more concentrated acids, which is discussed also in section 5.4.4.

5.4.1. Acid Concentration in the Presence of Biomass.

The cations present in lignocellulosic materials, such as Ca²⁺, Mg²⁺, and Mn²⁺ neutralize the acid. In order to know the efficient acid concentration, the effect of the neutralization capacity of the biomass should be taken into account. There are only a few publications in which this has been performed,^{46,50} but in many cases the neutralization effect of the biomass has been omitted. The neutralizing abilities of different wood materials have been reported to vary from 3.5 mg of H₂SO₄/dry wood.⁵⁰ Thus the acid concentration should always be corrected by taking into account the neutralization effect of the

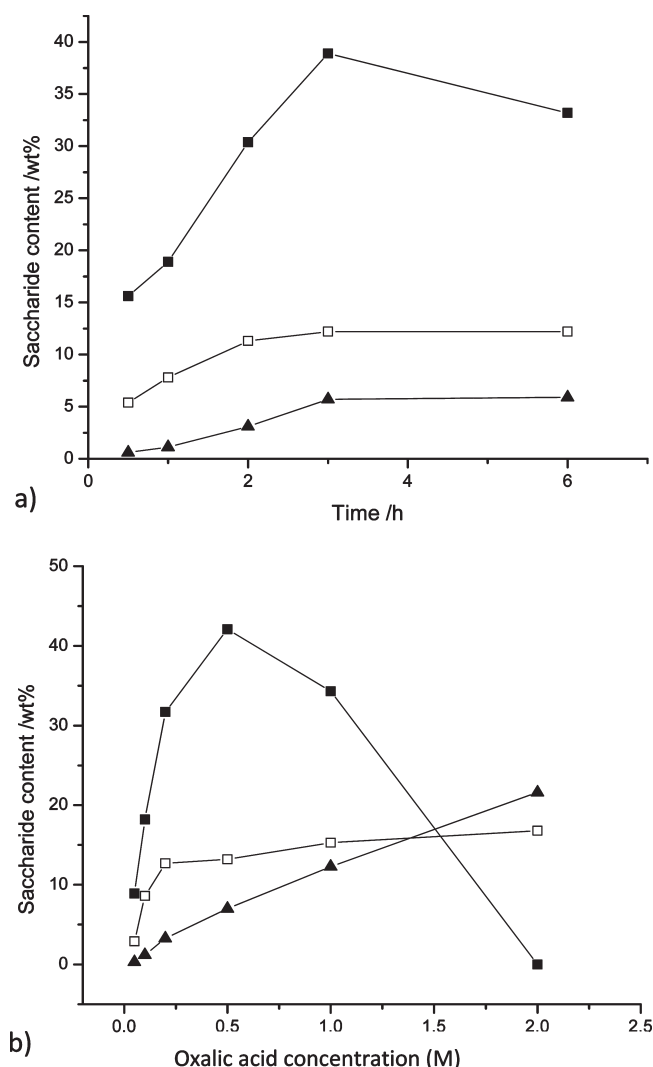


Figure 13. Acid hydrolysis of envelopes of corn grains (a) using 0.1 M oxalic acid as a catalyst as function of time and (b) as function of oxalic acid concentration after 60 min. Temperature 100 °C. Symbols: (□) L-arabinose, (▲) D-xylose; (■) xylooligosaccharide. Adapted from ref 76.

biomass. Principally, the neutralization capacity of the biomass can be determined by burning the biomass at 525 °C and titrating the ash with dilute sulfuric acid.⁹⁸ The neutralization capacity varies for different biomass types; for example, poplar has a higher neutralization capacity than paper birch.⁴⁶ The high neutralization capacity of poplar is related to its high ash content.

5.4.2. Dissociation of Acids at High Temperatures. The dissociation of sulfuric acid is reduced at high temperatures.⁹⁹ The determination of pH is not reliable at high temperatures, and thus the hydronium ion activity should be estimated.⁹⁴ Models have been derived for the hydrogen ion activity that take into account both the neutralization capacity of the biomass and the temperature.⁹⁹ It is, however, stated that sulfuric acid and hydrochloric acid are mostly dissociated at 200 °C.²⁴⁹

5.4.3. Reaction Order with Respect to Acid Concentration. The reaction order in dilute acid hydrolysis of hemicelluloses with respect to acid concentration is equal to one,²⁵⁰ and when hemicelluloses are soluble a first-order kinetics is suitable.⁷⁹ There have, however, been slight variations in experimentally reported values because errors can occur when the neutralizing capacity of

biomass has not been taken into account or, alternatively, reduced dissociation of sulfuric acid occurs at higher temperatures. This was also the case in acid hydrolysis of *O*-acetyl galactoglucomannan at 90 °C in the pH range of 1–2 using HCl as a catalyst (Figure 12).¹⁴² The first-order kinetic model also described well the kinetic data from the acid hydrolysis of arabinogalactan⁷⁹ and cellulose hydrolysis at 160 °C using different acids as catalysts.¹³³

5.4.4. Effect of Acid Concentration on Hydrolysis Selectivity. The acid concentration affects the hydrolysis selectivity in several ways, such as influencing the product distribution via formation of oligomers in the beginning of the reaction. Oligomers react further to monomers. Second, selective cleavage of side groups can be achieved especially when diluted acids are used as catalysts.^{52,76,78,79} The acid strength also affects the ratio of the dissolved cellulose to hemicellulose, the amount of lignin dissolved, and the decomposition of sugars, which is more pronounced under the influence of strong acids.⁵²

Oligomer formation takes place at the beginning of the reaction. Their further reaction to monomers is affected by the acid strength.⁵² The oligomer formation is more prominent in case of dilute acids,^{74,76,89} which was observed when diluted sulfuric acid was used for dissolution of hardwood, in which case a large fraction of xylan remained in polymeric and oligomeric form.⁷⁴ Analogously, in mild acid hydrolysis of corn grain envelopes with 0.05 M HCl at 100 °C during 3 h, 65% of the dissolved material was in form of xylooligosaccharides.⁷⁶ A comparative study of the product distribution using two different acid concentrations was performed in acid hydrolysis of wheat straw at 99 °C.⁵² Only a few percent of xylodextrins were present in the hydrolysate with 0.1 M TFA as a catalyst for 3 h, whereas no xylodextrins were observed for 5 M TFA at 70 °C for 24 h. This result indicated that oligomer decomposition as expected was enhanced in concentrated acid solutions. Oligomers can be separated by using filtration or membranes.⁷⁶

Selective release of the side chain sugars in hemicelluloses, such as rhamnose from gum arabic and arabinose from arabinoxylans⁷⁶ and arabinogalactan,⁷⁹ is facilitated with diluted acids as catalysts. For strong acid solutions, such as 1–2 M HCl or 1.5 M H₂SO₄, acid hydrolysis of gum arabic at 100 °C became less selective toward the release of rhamnose, which is in the side chain of the galactose backbone.⁷⁷ At the same time, due to high galactose content of the hydrolysate, the purification of rhamnose became more expensive.⁷⁷ Analogously to these results, also selective acid hydrolysis of envelopes of corn grains containing arabinose linked to the xylan backbone (see section 2.2.) was performed at 100 °C using diluted sulfuric, oxalic, or hydrochloric acids as catalysts. The highest arabinose yield obtained using 2 M oxalic acid as a catalyst (Figure 13b) was about 16 wt %.⁷⁶ Arabinose, which is in the side chain of arabinoxylan, was released from wheat straw at 99 °C slightly faster, showing the yield of 2.6% after 7 h with 1 M TFA compared with 2% for 0.1 M TFA.⁵² One drawback of dilute acids is that if the acid concentration is too low, the process becomes economically unfavorable,⁷⁶ and thus the selection of acid concentration should be optimized to achieve high enough rates for selective hydrolysis of selected sugars without losing the process efficiency.

Selective acid hydrolysis of hemicelluloses prior to cellulose dissolution is also affected by the acid strength.⁵² When hydrolyzing wheat straw at 99 °C for 23 h with 1 M TFA, since the hydrolysis of cellulose was very limited,⁵² the glucose yield was only below 1%, whereas the corresponding xylose yield was 22% after 7 h. When this result is compared with the corresponding one using 0.1 M TFA, the xylose yield was only 16%, but no glucose was released.

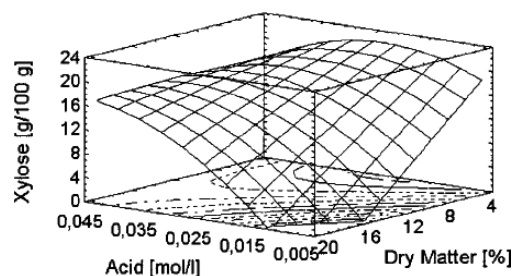


Figure 14. Effect of acid concentration and initial concentration of biomass on xylose yield in acid hydrolysis of sugar cane bagasse at 130 °C in 10 min.⁸⁹ Reprinted with kind permission from Springer Science & Business Media.

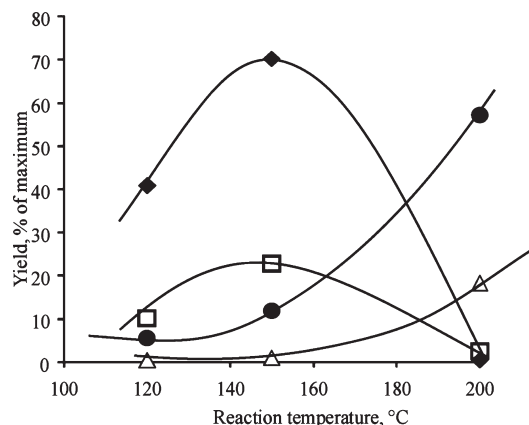


Figure 15. The yield of hexoses, pentoses, hydroxymethylfurfural, and furfural from the acid hydrolysis of Loblolly pine sawdust with trifluoroacetic acid at pH of 1.65 for 60 min. Symbols: hexoses (\square); pentoses (\blacklozenge); HMF (\triangle); furfural (\bullet).⁶⁰ Reprinted with permission from American Chemical Society.

Sugar decomposition is an undesired reaction, which occurs at high temperatures after prolonged hydrolysis times and with more concentrated acids. When the acid concentration is too high, degradation of sugars takes place; for example, 5-hydroxymethyl-2-furfural and furfural are formed from hexoses and pentoses, respectively.⁶⁰ A linear relationship has been observed between the xylose decomposition and the acid concentration in the acid hydrolysis of different wood chips with sulfuric acid.¹¹³

Lignin decomposition products are formed to a minor extent when the acid concentration is increased, since when brewer's spent grain was hydrolyzed by sulfuric acids with the concentrations of 100 mg/g and 140 mg/g at 120 °C, the concentration of lignin degradation products after 17 min reaction time decreased from 4.22 to 2.7 g/dm³.³⁶² Analogously, it has also been observed that the lignin becomes more insoluble when the acid concentration is increased.²³⁰ The reason for the above-mentioned results is that in more concentrated acids condensation of lignin compounds occurs making lignin structure more rigid.

In dilute acid hydrolysis of cellulose, the selectivity for glucose decreased with increasing acid concentration. The yield of 5-hydroxymethylfurfural was less than 10% when cellulose was hydrolyzed with 0.05 wt % sulfuric acid below 225 °C.¹³² Among other side products, levoglucosan and cellobiose should be mentioned, although their amount was maximally below 5%. Analogously in ref 128, diluted sulfuric acid was used as catalyst for hydrolysis of cellulose in bagasse at 180–220 °C giving maximally about 55% yield of glucose. A very high glucose yield,

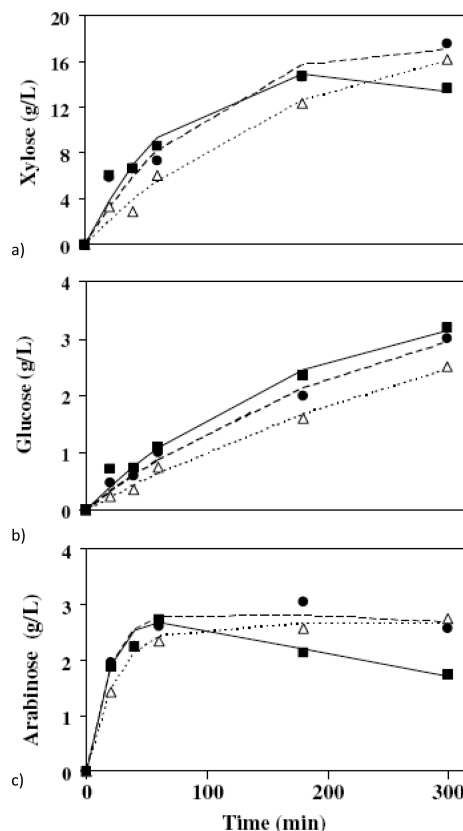


Figure 16. The yields of xylose, glucose, and arabinose in acid hydrolysis of sugar cane bagasse at 122 °C using phosphoric acid with different concentrations as a catalyst. Symbols: (\triangle) 2 wt %; (\bullet) 4 wt %; (\blacksquare) 6 wt %.⁵⁵ Reprinted with permission from Elsevier.

of about 90%, was reported in acid hydrolysis of cellulose using 2.5 wt % phosphoric acid as catalyst at 175 °C,¹³⁵ although it should not be forgotten that nearly quantitative saccharification of Douglas fir was achieved via application of a two-step method using strong and diluted sulfuric acids at 30 and 121 °C, respectively, for its dissolution (see section 4.3.1).²³⁶

Recently, cellulose dissolution has also been investigated in different ionic liquids using diluted mineral acids as catalysts.¹²⁵ The dissolution temperature was only 90 °C, and about 58% of cellulose was converted to glucose after 30 min in 25 mL of [EMIM][Cl] as an ionic liquid and 1 mL of 50 wt % sulfuric acid as a catalyst. Also nitric acid and trifluoroacetic acid were used as catalysts. The total saccharification and homogeneous dissolution of lignocellulosic materials with strong acids¹²⁶ are briefly reported in section 8, but they are not the main emphasis of this work.

5.5. Effect of Solid Concentration

Solid concentration can affect not only hydrolysis selectivity,^{51,89} but also the process economy, meaning that when very diluted solid solutions are hydrolyzed, much energy is needed for their reconcentration.⁷⁶ An increased solids concentration in acid hydrolysis of oak,⁵² spruce,⁷¹ and sugar cane bagasse⁸⁹ decreased the selectivity toward hemicellulose dissolution, since more cellulose was dissolved with high initial solid concentrations. For example, the xylose yield decreased with an increasing solid content in the acid hydrolysis of oak hardwood with sulfuric acid at 140–180 °C.⁵² In acid hydrolysis of spruce, less selective

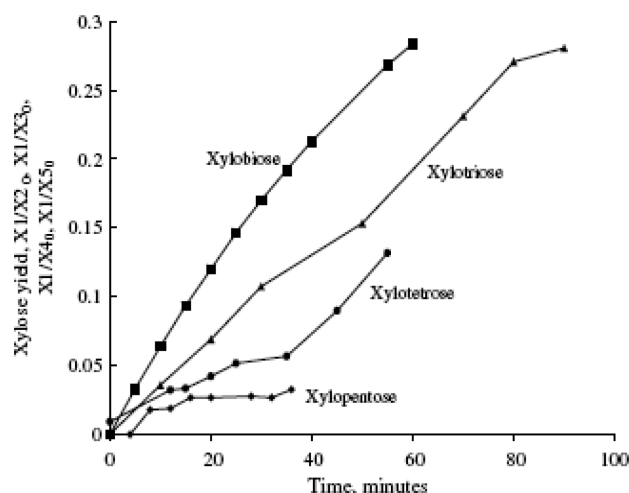


Figure 17. Xylose yield in acid hydrolysis of xylooligosaccharides with DP varying in a range of 2–5 using sulfuric acid as a catalyst at pH 4.75 and 160 °C.¹⁰¹ Reprinted with permission from Elsevier.

hydrolysis toward mannose was achieved using high solid to liquid ratio (Figure 9).⁷¹ In acid hydrolysis of sugar cane bagasse, the maximum xylose yield was plotted as a function of the initial acid concentration as well as a function of the dry matter (Figure 14), thus showing that the maximum sugar content results from a combination of several parameters, such as the acid and solid concentrations.⁸⁹ The best xylose yields were achieved by using small amounts of solid material in the acid hydrolysis and not too high initial acid concentrations. Under these conditions, certainly the economical feasibility of the process is not very good, and the process needs to be carefully optimized. Additionally, the lignin dissolution was dependent on the solid to liquid ratio as follows: the formation of soluble lignin decomposition products increased with a decreasing liquid-to-solid ratio, but the reason for this has not been clarified.⁶²

5.6. Sugar Decomposition Kinetics

The sugar decomposition kinetics is affected by the acid hydrolysis time, temperature, and acid type and concentration, which have been reviewed above. When the severity of the hydrolysis conditions is increased, the sugar degradation becomes more profound. Moreover, the acid type affects the decomposition kinetics (see section 5.3.1.2). Monosaccharides undergo degradation to aldehydes at high temperatures,^{72,91} which decreases their yields. At the same time, the sugar hydrolysate is discolored, thus increasing the costs for decolorization of sugars and purification by chromatographic techniques.⁷⁶ At high temperatures, hexoses dehydrate to 5-hydroxymethylfurfural, whereas furfural is formed via dehydration of pentoses, such as from xylose.^{72,91} This was clearly noticed in the decreased yields of hexoses and pentoses obtained with increasing temperature by acid hydrolysis of Loblolly pine sawdust using trifluoroacetic acid as a catalyst (Figure 15).⁶⁰ It was, however, stated in ref 72 that arabinose and glucose recoveries from the hydrolysates of sugar cane bagasse were complete even at temperatures above 160 °C.⁷²

In addition to these parameters, the sugar structure affects its decomposition rate.¹⁰⁰ It is known that pentoses, for example, xylose, are decomposed faster to furfural than hexoses, such as mannose, to hydroxymethylfurfural. The slowest decomposition rate was achieved for glucose.¹⁰⁰ This fact also explains the result

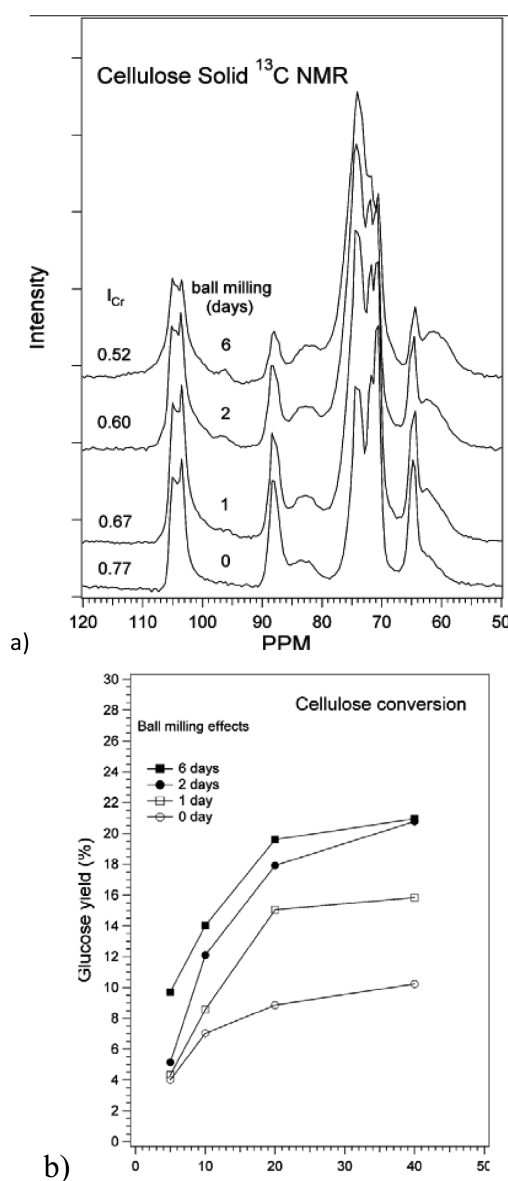


Figure 18. (a) The XRD patterns for α -cellulose as received and after ball milling for 1, 2, and 8 days and (b) the yields of glucose from the α -cellulose in panel a, using 0.05 M sulfuric acid at 175 °C.¹⁵⁹ Reprinted with permission from American Chemical Society.

showing that the optimum temperature for maximizing the yields of xylose and mannose are lower than that for glucose (see section 5.2.1).⁷¹ Arabinose is decomposed easier than xylose, which can be seen by comparing panel c with panel a in Figure 16. This result indicated that furfural formation mainly originated from arabinose decomposition and to a minor extent from xylose decomposition,⁵⁵ when sugar cane bagasse was hydrolyzed with phosphoric acid at 122 °C. On the other hand, the total arabinose release was at about the same level independently on the hydrolysis conditions from rice straw, when the hydrolysis was performed at 121 °C using 1–1.4% sulfuric acid as catalyst⁸⁵ indicating that arabinose was not dehydrated under these conditions. By comparison of these two cases, it can be stated that the main differences are in the acid type and concentration, since the major arabinose decomposition was observed when 6 wt % phosphoric acid was used as a catalyst (Figure 16),

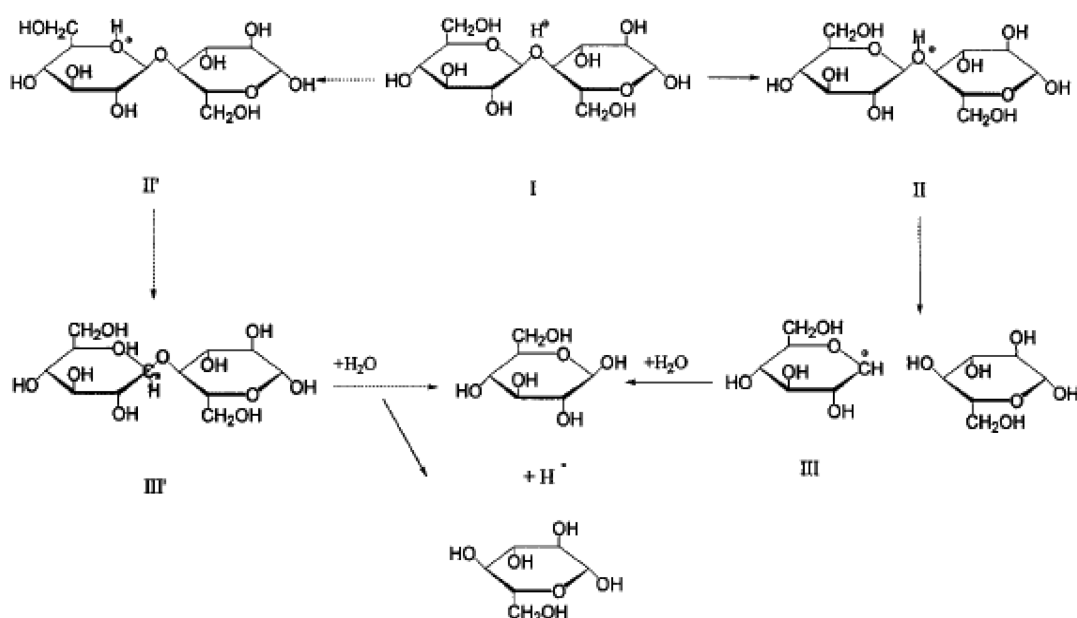


Figure 19. A proposed mechanism of acidic hydrolysis of glycosidic linkages.¹³⁸ Reprinted with kind permission from Springer Science & Business Media.

indicating that the acid concentration was crucial for arabinose degradation.⁵⁵

Secondary side reactions starting from 5-hydroxymethylfurfural are formation of levulinic and formic acid.⁷¹ It was, however, pointed out, that also other side reactions can take place, but the kinetics of the acid hydrolysis of lignocellulosic material mainly consists of cellulose and hemicellulose dissolution to oligosaccharides and in the second step to sugars, which in turn decompose further.

In dilute acid hydrolysis of cellulose, sugar dehydration occurred when applying higher temperatures and phosphoric acid concentrations than 175 °C and 2.5 wt %, respectively.¹³⁵ It was also stated that when grass and cellulose hydrolysis were compared, pentoses were observed to be more prone to the dehydration than hexoses.¹³⁵

5.7. Kinetic Studies with Model Compounds

Kinetic studies have been performed with model compounds, such as xylooligosaccharides¹⁰¹ and glycosides,²³⁸ with the aim to obtain more detailed kinetic information on how the structures of the sugars or oligomers affect the reaction rate and selectivity.

Xylooligomers having the degree of polymerization (DP) in a range of 2–5 were applied as a raw material in acid hydrolysis using sulfuric acid as a catalyst.¹⁰¹ The idea was to assess which steps were involved in xylose degradation to furfural.¹⁰¹ The acid hydrolysis was performed with dilute sulfuric acid at 160 °C by varying the pH from neutral to 1.45. The formation of xylose from different xylooligomers is demonstrated in Figure 17, showing that the reaction rate increased with decreasing DP.¹⁰¹ Analogously to the results in ref 101, the rate for the nonreducing end-group is higher than that for the other bonds, since the acid hydrolysis rate of xylobiose is about 1.8 times higher than that of the internal xylooligosaccharide.³¹ It was observed in the work of ref 101 that the oligomers of DP 4 and 5 did not degrade, whereas the dimers and trimers degraded already in the absence of the acids to undesired products. Additionally, lower xylooligomers with DP of 2–3 degrade directly to furfural and form xylose in corn cob autohydrolysis.²⁵¹ Sulfuric acid has been found to be a selective catalyst in the xylobiose hydrolysis.⁹⁸

In a model study, the acid hydrolysis of glycosides was investigated to get information about the hydrolysis activity of different sugar units. The following increasing order for the hydrolysis of methyl glycosides has been reported: glucoside < mannoside < galactoside < xyloside < arabinoside.²³⁸

5.8. Effect of Cellulose Structure on the Hydrolysis Rate

The acid hydrolysis of cellulose differs from that of hemicelluloses due to the crystallinity in cellulose as discussed in section 2.1. The rate of acid hydrolysis of crystalline cellulose is 1–2 orders of magnitude lower than that of the soluble model compounds.¹³⁸ For example, the treatment of microcrystalline cellulose with 86 wt % phosphoric acid is a very rapid process.^{252,268} In addition to crystallinity also swelling of cellulose affects its hydrolysis rates.¹⁸ Crystallinity, typically given as crystallinity index (CrI),²⁵³ has been studied by different methods, such as X-ray diffraction and ¹³C nuclear magnetic resonance (NMR). In reality substrate accessibility is more important than CrI per se. Thus different hydrolysis rates for different cellulose can be explained by substrate accessibility,²⁵⁴ and the role of CrI has been criticized in several reviews^{255,256} since the measurement of CrI is also very tricky.²⁵⁷ The effect of crystallinity in α -cellulose on its hydrolysis rate has been systematically investigated in ref 21. α -Cellulose and ball-milled α -cellulose were hydrolyzed with 0.05 M sulfuric acid at 175 °C, and the crystallinity was determined by X-ray diffraction (XRD). It should be pointed out here, that ball-milling also affects the substrate accessibility. The cellulose crystalline plane 002 is visible at $2\theta = 22.6^\circ$ (Figure 18a),²⁵⁸ and the intensity of this peak decreased with increasing ball milling time for α -cellulose. When α -cellulose, either as received or ball-milled for different times, was hydrolyzed with diluted sulfuric acid, the results revealed that the glucose yield increased by a factor of 2.4 using ball milling pretreatment for cellulose (Figure 18b). Thus it was concluded that the degree of crystallinity strongly affects the hydrolysis rate being most probably an exception in light of other work on this subject. For instance, a good example against the role of CrI is hydrolysis of high crystallinity bacterial cellulose

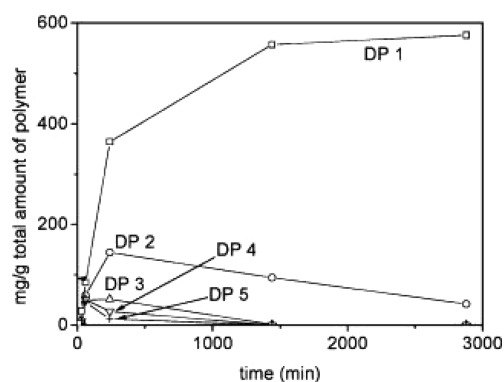


Figure 20. Kinetics for the formation of oligomers in the acid hydrolysis of O-acetylgalactoglucomannan at pH 1 at 90 °C.¹⁴² Reprinted with permission from American Chemical Society.

(high CrI and high surface) in comparison with microcrystalline cellulose (modest CrI and low surface). The hydrolysis rate of bacterial cellulose is much faster than that of Avicel, which cannot be explained by CrI but rather by substrate accessibility.

The dissolution temperature of crystalline cellulose was recently investigated by *in situ* optical microscopy showing that it declined as a function of sulfuric acid concentration. In the absence of sulfuric acid, it dissolved at 297 °C, whereas with 20 M sulfuric acid, the dissolution temperature of crystalline cellulose was 273 °C.¹²⁴

6. MECHANISM OF ACID HYDROLYSIS OF HEMICELLULOSES

The mechanism of acid hydrolysis of glycosidic bonds is shown in Figure 19. It occurs via protonation either of the glycosidic bond or of pyranic oxygen.²³⁹ The formation of cyclic pyranic oxygen was proposed in ref 259, although it was pointed out in ref 4 that the formation of a cyclic intermediate needs conformational changes of the tetrahydropyran ring and that this route needs more energy compared with the acyclic route.²⁶⁰ Acid-catalyzed hydrolysis of cellulose is believed to occur analogously to the acid hydrolysis of disaccharides starting with a proton that is interacting with the glycosidic oxygen linking two sugar units (Figure 19).⁴ As a consequence, conjugate acid is formed. Thereafter the C—O bond is cleaved and the conjugate acid forms a carbenium ion. This unimolecular step is crucial in the mechanism. The free sugar is formed in the next step via rapid addition of water and liberation of the proton. This mechanism is the basis for a two-step pseudohomogeneous first-order reaction system.¹⁰⁰

From the mechanistic point of view, it is also interesting to know that the acid hydrolysis rate of hemicelluloses varies depending on their structure. Both random scission^{68,80} and selective scission of the side chain have been reported.^{77,79} A random scission of O-acetylgalactoglucomannan has been proposed by ref 80 because the rates for formation of oligomers with DP 2–5 were about the same in a range of 0.3–0.5 mg/(g min) (Figure 20). Furthermore, acid hydrolysis of xylan was reported to be random,⁶⁸ whereas in the selective acid hydrolysis of the vegetable fibers, L-arabinose was selectively cleaved by using dilute acids as catalysts.⁷⁶ Analogously to the release of arabinose also rhamnose can be selectively cleaved starting from gum arabic by using dilute sulfuric acid as a catalyst,⁷⁷ since rhamnose is in the side chain of the galactose backbone (see section 2.2). Furanosides hydrolyze faster than pyranosides.²⁶¹ The reasons for this can be that

hydrolysis rate is faster for glycosidic linkages exhibiting non-reducing ends.²⁶² Terminal linkages also hydrolyze faster than others.²⁶¹ It was also concluded in ref 36 that different functional groups in hemicelluloses exhibit different reactivities.

7. MODELS FOR ACID HYDROLYSIS OF HEMICELLULOSES AND MODELS FOR MOLECULAR WEIGHT DISTRIBUTION

Kinetic modeling of the acid hydrolysis of hemicelluloses has been summarized in ref 111 and developed in several publications.^{24,28,30,46,72,79,80,113,263} In acid hydrolysis of biomass and hemicelluloses, the challenge is to analyze also the oligomers and take their role into account in the kinetic modeling. This has been performed in refs 56, 79, 80, and 93, but there are also several publications where no oligomer analysis has been performed and their part has been omitted in the kinetic model.^{30,46,72,113} Furthermore, when the lignocellulosic material exhibits a heterogeneous structure being both crystalline and noncrystalline, it is clear that the kinetic model is more complicated and a simple-first order model will not work. When, however, the material has converted to a homogeneous solution, hydrolysis can be treated with first-order kinetics. Initially, the hemicellulose attack occurs randomly by the acid. The hydrolysis rate of oligomers depends on the DP (see section 5.7). This makes developing kinetic models demanding, since it is difficult to measure accurately the oligomer concentrations. It is known that the hydrolysis rate at the nonreducing end group is higher than at the other bonds.³¹

Due to the biphasic nature of lignocellulosic biomass, specific kinetic models have been developed for acid hydrolysis of biomass. It has been observed that one part of xylan reacts rapidly, whereas the rest was called slow-reacting xylan.⁵⁰ There are also publications in which the molecular mass distribution has been taken into account and corresponding kinetic models have been developed.^{79,80} In addition to the models derived for the formation of oligomers, sugars, and dehydration products, modeling has been performed also for deacetylation and formation of soluble lignin. More complicated kinetic models, which are quite complex due to the semicrystalline structure of cellulose, have also been developed for cellulose dissolution.^{148,242} The complexity of the models originates from the fact that both physical and chemical phenomena control the overall rate and efficiency. These models include in addition to glucose disaccharides, anhydrosugars, and degradation products,¹⁴⁸ and nonlinearity has also been described by approximate solutions.²⁴³ Autocatalytic acid hydrolysis of cellulose with crystalline and amorphous fractions was described in ref 241. Furthermore, models taking into account both heterogeneous hydrolysis and transport processes for dissolution of microcrystalline cellulose have been developed.²⁴¹ Since cellulose dissolution is not the main emphasis in this work, but rather the dissolution of hemicelluloses is, these models have not been described here in more detail.

7.1. Model with Fast- and Slow-Reacting Xylan

When the process is described by a simple consecutive reaction route, only the decomposition of lignocellulosic material to sugars and their further decomposition have been taken into account.³⁰ It has, however, been stated that at high temperatures (>160 °C), the sequential first-order kinetics is valid, while the hydrolysis is not homogeneous at lower temperatures. This implies that one part of the hemicelluloses undergoes rapid hydrolysis, whereas the other part hydrolyzes slowly.^{46,50,72,127,250,264} Furthermore, the fraction

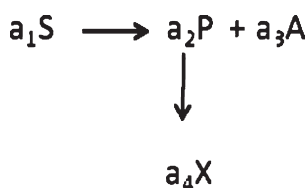


Figure 21. Reaction scheme for dilute acid hydrolysis of wheat straw adapted from ref 56.

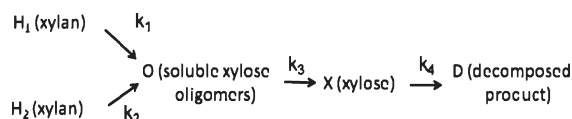


Figure 22. Biphasic reaction network for fast- and slow-reacting xylan adapted from ref 93.

of the slowly reacting part has been estimated to be about 0.2–0.32 (see section 5.2.2.).⁵⁰ Thus for xylan hydrolysis the following kinetic model was proposed:⁴⁰

$$R_x = zk_f X_f + (1 - z)k_s X_s \quad (1)$$

in which xylan was divided into the fast- and slow-reacting fraction, corresponding to their rate constants, k_f and k_s , respectively. The z is the solid residue of xylan. Furthermore, the apparent (or lumped) rate constants for fast- and slow-reacting xylan were defined according to a modified Arrhenius' equation as follows:

$$k_f = k_{f,0} \left(-\frac{E_f}{RT} \right) C_H^m \quad (2)$$

$$k_s = k_{s,0} \left(-\frac{E_s}{RT} \right) C_H^n \quad (3)$$

in which E_f and E_s are the apparent activation energies for fast- and slow-reacting xylan and C_H is the hydrogen ion concentration. The exponents m and n are empirical rate parameters determined via fitting with their typical values of 0.93 and 1.02, respectively, being, as expected, not far from unity. An analogous model was used in ref 46 in the acid hydrolysis of switchgrass, poplar, and corn stover.

7.2. Kinetic Models Including Oligomer Concentrations

A kinetic model including the oligomer concentration has been developed for the acid hydrolysis of wheat straw hemicelluloses to produce xylose and arabinose by using dilute sulfuric acid in the temperature range of 34–90 °C.⁵⁶ The reaction scheme for dilute acid hydrolysis of wheat straw, which is composed of arabinoxylans (see section 2.2), is presented in Figure 21, in which S and P denote hemicelluloses and polymeric species not containing arabinose, respectively. Furthermore, A and X are arabinose and xylose. The rate equations are written following the first-order kinetics:⁵⁶

$$-r_s = K_1 c_s \quad (4)$$

$$-r_A = dc_s/dt \quad (5)$$

$$r_p = \beta K_1 c_s - K_2 c_p \quad (6)$$

$$r_x = \gamma K_2 c_p \quad (7)$$

where $K_1 = a_1 k_1$, $K_2 = a_2 k_2$, and $\alpha = a_3 M_A / (a_1 M_P)$, $\beta = a_2 M_P / (a_1 M_s)$, $\gamma = a_4 M_x / (a_2 M_P)$, with M_i denoting molecular mass of

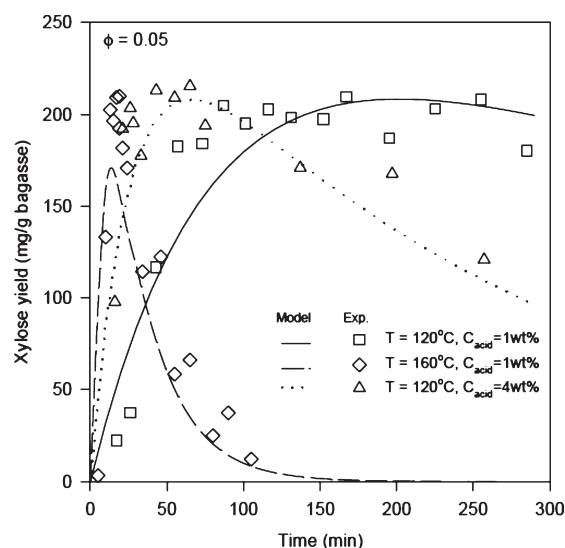


Figure 23. Effect of temperature and acid concentration in acid hydrolysis of sugar cane bagasse with sulfuric acid.⁷² Reprinted with permission from Elsevier.

compound i . Furthermore, α , β , and γ denote the contents of arabinose in hemicellulose, xyloextrin, and xylose in xyloextrins, respectively.⁵⁶ Furthermore, the dependence of the rate constant on the acid concentration is given by

$$K_i = K_{i,0} C_H^{n_i} \quad (8)$$

in which C_H is the acid concentration (g/L) and n_i is the reaction order. The reaction orders were 1.09 and 1.63 for the steps 1 and 2, respectively. The parameter values were determined, and the model fit was very good (degree of explanation was not given). The main products were xylose and arabinose. Maximally about 1% xyloextrins were formed, but they were further decomposed to xylose.⁵⁶

Another model for xylan hydrolysis via biphasic decomposition has been proposed by Chen et al.⁹³ according to Figure 22, since in a semilogarithmic plot of $\ln c_{xylose}/c_{0,xylan}$ versus time a fast and a slow decrease of xylan concentration was observed (the picture is not depicted here). Thus the following rate equations were derived for xylan oligomers and xylose:

$$\frac{dH_1}{dt} = -k_1 H_1 \quad (9)$$

$$\frac{dH_2}{dt} = -k_2 H_2 \quad (10)$$

$$\frac{dO}{dt} = k_1 H_1 + k_1 H_2 - k_3 O \quad (11)$$

$$\frac{dX}{dt} = k_3 O - k_4 X \quad (12)$$

where H_1 and H_2 represent the fast- and slow-reacting fraction of xylan. O stands for oligomers, X for xylose, and D for decomposed products. Analytical solutions for the first differential equations can be derived, and the fitting is shown in Figure 23. An analogous model was tested by Lavarack et al.⁷² in the acid hydrolysis of sugar cane bagasse, but according to their investigation, a better fit compared with the above-mentioned one was achieved with a simple consecutive mechanism, in which xylan was hydrolyzed to xylose in the first step, followed by its decomposition.

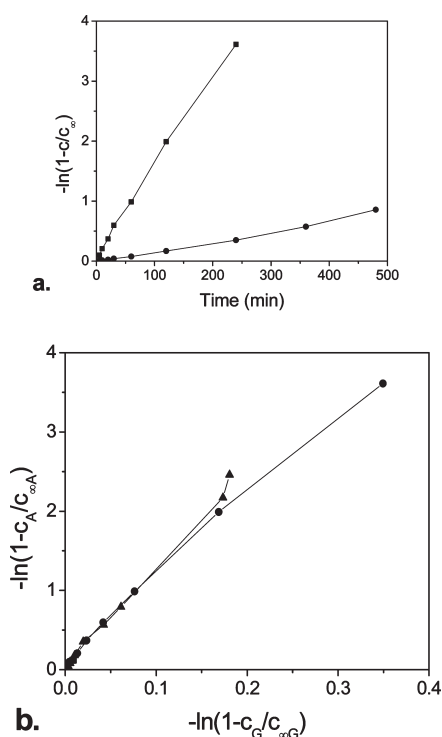


Figure 24. First-order kinetic model applied for acid hydrolysis of arabinogalactan, (■) arabinose and (●) galactose, and (b) double logarithmic plot for the determination of kinetic constants, (●) pH 1, (▲) pH 2, and (■) pH 3. Adapted from ref 74.

Kinetic models have also been developed for acid hydrolysis of xylooligomers.^{31,101} Several types of models have been tested in ref 101, such as oligomer degradation directly to other products and lower oligomers or alternatively oligomers reacting only to lower oligomers. The latter model fitted better to the kinetic data, indicating that the higher oligomers of DP 4–5 do not decompose directly but only react to lower oligomers. For the lower oligomers of DP 2–3, however, the direct decomposition was also taking place, in addition to formation of xylobiose and monomers.

7.3. Kinetic Modeling of Acetic Acid Formation

Acetic acid is formed via acid hydrolysis of the acetyl groups in hemicelluloses. Since acetic acid is not decomposed under the conditions in which lignocellulosic materials have been hydrolyzed,²⁶⁵ the following first-order kinetic model for formation of acetic acid was proposed:

$$-r_{\text{AcH}} = -kc_{\text{Ac},0} \quad (13)$$

in which $c_{\text{Ac},0}$ denotes the initial concentration of acetyl groups.^{55,91} On the other hand, in ref 50, the determined acetyl removal data scattered too much, and thus no modeling was performed.

7.4. Kinetic Modeling of the Acid-Soluble Lignin

Solid lignin is degraded under acidic conditions to form acid-soluble lignin, which can further decompose to small products. They can, however, react reversibly to form acid-soluble lignin. The kinetics of formation of the acid-soluble lignin is as follows: it is initially formed very rapidly, but its concentration reaches a plateau level already after 350 min.⁷² An analogous mechanism has been proposed by Allen et al.²⁶⁶ in which lignin initially depolymerizes and in the consecutive step it condenses or repolymerizes after prolonged reaction times. During the

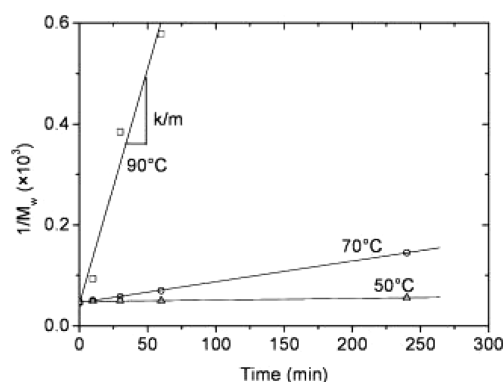


Figure 25. $1/M_w$ is plotted as a function of hydrolysis time and the kinetic parameters k/m can be determined in the acid hydrolysis of *O*-acetyl galactoglucomannan at pH 1 at different temperatures.¹⁴² Reprinted with permission from American Chemical Society.

repolymerization large amounts of insoluble residual lignin are formed.

7.5. Kinetic Model for Acid Hydrolysis of Arabinogalactan

A kinetic model for acid hydrolysis of arabinogalactan in the presence of HCl (see sections 4.3.3 and 4.3.4) has been presented as follows;⁷⁹

$$r_A = k_1 c_H C_{A,AG} \quad (14)$$

$$r_G = k_1 c_H C_{G,AG} \quad (15)$$

in which c_A and c_G denote the arabinose and galactose concentrations, while $c_{A,AG}$ and $c_{G,AG}$ are the concentrations of arabinose and galactose present in the arabinogalactans at time t . The acid catalyst concentration (c_H) was assumed to be constant during the hydrolysis process. The model was checked with a logarithmic plot originating from the solved first-order differential equations,

$$-\ln(1 - c_A/c_{\infty A}) = (k_1/k_2)\ln(1 - c_G/c_{\infty G}) \quad (16)$$

in which c_A and c_G are the concentrations of arabinose and galactose at time t , and $c_{\infty A}$ and $c_{\infty G}$ are the respective concentrations after prolonged reaction time, corresponding to true conversion. The first-order kinetic plots together with the double logarithmic plot of arabinose versus galactose kinetics are shown in Figure 24, panels a and b, respectively. The latter one was used for determination of rate constants.

7.6. Model for Acid Hydrolysis of *O*-Acetyl galactoglucomannan Taking into Account Average Molecular Mass

In the acid-catalyzed hydrolysis of *O*-acetyl galactoglucomannan using HCl as a catalyst (see section 4.3.2), the following model was developed:¹⁴²

$$k_w(\text{pH}) = k_y^0 + k_w^0 [\text{H}^+] \quad (17)$$

in which the apparent reaction rate constant was proportional to the acid concentration. k_y^0 and k_w^0 denote intercept and slope in Figure 25.

The molar mass at time t , M_t , was correlated with the initial molar mass M_0 , the apparent activation energy E , monomer molar mass m and time t as follows:

$$\frac{1}{M_t} = \frac{1}{M_0} + \frac{A e^{-[E/(RT)]t}}{m} \quad (18)$$

By taking into account the effect of pH, the following equation for the molar mass at time t was derived:⁷²

$$\frac{1}{M_t} = \frac{1}{M_0} + \frac{(k_y^0 + k_w^0[\text{H}^+])}{m} e^{-[E/(RT)]t} \quad (19)$$

The inverse of the molecular weight was plotted versus time (Figure 25), and it was possible to obtain k/m as a slope. Thereafter, the reaction rate constants at different pH were calculated and the apparent activation energies were determined using Arrhenius' equation. For *O*-acetylgalactoglucomanan, the apparent activation energy was 150 kJ/mol (Table 3, entry 3).

8. TECHNOLOGY DEVELOPMENT IN WOOD SACCHARIFICATION

The first process, the Scholler process, for wood saccharification was developed in the 1920s, and after that several processes have been developed. They use sulfuric acid,⁵⁸ hydrochloric acid,⁶³ or hydrofluoric acid⁶⁷ as catalyst. Furthermore, both batch⁶³ and continuous⁵⁸ operations, as well as a two-stage process,³⁴ have been developed.

The Scholler process applies dilute sulfuric acid as a catalyst at 170 °C for wood saccharification. Typically reaction time of 45 min is used for hydrolysis, and after neutralizing the acid, the yield of fermentable sugars is about 50%.²⁶⁷ A continuous process applying principally the Scholler process conditions was developed by Madison.³⁵ The benefit of this process compared with the Scholler process was the fact that it was possible to remove and suppress the degradation of sugars. The optimum residence time for hydrolysis of Douglas fir wood waste was 2.8 h giving 244 L of 95% ethanol from one ton of wood waste.³⁵ A plug flow reactor was used acid hydrolysis of purified cellulose at 240 °C using 1 wt % sulfuric acid as a catalyst and with a residence time of 0.22 min about 50% of the potential glucose amount was obtained.¹⁰⁵ The idea in the two-step process using sulfuric acid as a catalyst³⁴ was to hydrolyze hemicelluloses in the first step at 170 °C, whereas cellulose was hydrolyzed at 190 °C in the second step. The degradation of pentoses was suppressed, because they were removed prior to the second step. After hydrolysis, the hydrolysate was neutralized and purified to remove some furfurals and other yeast inhibitors.⁶⁶

The processes using HCl as a catalyst were the Bergius process⁶³ and the Noguchi process.⁶⁴ In the former process, the hydrolysis was performed with 12 M HCl at room temperature.⁶³ Typically 320 L of 95% ethanol was achieved from one ton of dry wood. The process economy is not very good due to the demand of corrosive resistant equipment and the expensive recovery of HCl. The hydrolysis rate was enhanced by using 6–7 mol/L HCl as a catalyst together with CaCl_2 or LiCl . The yield of glucose was about 85% of the theoretical one, when hydrolysis of cellulose was performed at 90 °C.¹¹⁹ In the Noguchi process prehydrolysis step, the gaseous HCl was adsorbed on the dried wood and the temperature was increased by applying steam at 100–130 °C. The dissolved sugars from hemicelluloses were extracted with water, and thereafter the wood particles were flash-dried by hot air. The dried wood particles were contacted with cold HCl gas during which the acid concentration reached a level of 42%. The Noguchi process applies at as low temperature as 45 °C using gaseous HCl as a catalyst. The yield of sugars was about 90% of the theoretical one.

Anhydrous HF was used as a catalyst in wood saccharification in Hoechst process.⁶⁷ Nearly complete acid recovery in this process could be realized due to the low boiling point of HF (19.5 °C). About 45% of the fermentable sugars were achieved at 0 °C.⁶⁵

The main drawbacks in acid hydrolysis of biomass based on the industrial knowledge are the large amount of solid waste formed and removal of sugar degradation products, if the main aim is to ferment sugars to ethanol.

9. CONCLUSIONS

The biorefinery concept to produce fuel components, platform chemicals, and fine chemicals from biomass is currently a hot topic, since mankind needs alternative carbon sources replacing oil. Biofuels have certainly a large impact, whereas high-value biochemicals are also essential for future economy. Biomass is an abundant renewable raw material in nature. A basic process in biorefinery is hydrolysis of cellulose and other biomass components to sugars, which can be performed in several ways. The acid hydrolysis of cellulose is not very selective due to the challenge of interrupting the reaction at the maximum sugar yield. Furthermore, it suffers other problems, such as corrosion, formation of large amounts of solid waste when using inorganic mineral acids as catalysts, etc. On the other hand, selective hydrolysis of hemicelluloses is an applicable method for producing sugars, since it can be performed rather selectively under mild conditions without dissolving cellulose. As raw materials, wood chips and agricultural and pulping wastes can be utilized.

The products from selective acid hydrolysis of biomass, in addition to glucose, include rare sugars, such as xylose, mannose, galactose, arabinose, and rhamnose, which either have already commercial applications or are potential intermediates for several applications areas in pharmaceutical and food products. Bioethanol production via acid hydrolysis of biomass followed by enzymatic fermentation of sugars to ethanol is already an existing technology having a huge economic impact. In addition to acid hydrolysis of hemicelluloses, comparison with cellulose acid hydrolysis has been performed.

The selective acid hydrolysis of hemicelluloses for the production of rare sugars can be optimized by selecting optimum temperature, acid strength, solid to liquid ratio, and hydrolysis time for the process. Under too harsh conditions, the selectivity for sugars declines due to several reasons, among them sugar decomposition and partial dissolution of cellulose. Furthermore, the selectivity to produce sugars located in the side chain of hemicelluloses can be tuned via selecting an optimum acid strength.

From the practical point of view, it should be stated that the process of producing rare sugars via dilute acid hydrolyses of lignocellulosic material is not yet fully realized, since it involves several separation, reconcentration, and purification steps for sugars, such as neutralization, filtration, precipitation by addition of anti-solvent or an organic solvent, in which lignin is soluble and sugars remain in the water phase, reconcentration of sugar solutions, discoloration, chromatographic separation, etc. Furthermore, when diluted soluble acid solutions are applied, their reconcentration and reuse are economically challenging. The downstream processing of the sugar solutions needs further research efforts on the way of utilizing hemicelluloses of biomass as a source of rare sugars.

Various kinetic models have been developed for acid hydrolysis of lignocellulosic material and hemicelluloses. These include either simply homogeneous first-order models or alternatively so-called slow- and fast-reacting fractions of xylan, which are simplified models taking into account the heterogeneity of the raw material. Furthermore, in more advanced models, where the oligomer analysis has been possible, formation and decomposition of oligomers has been also accounted for. In addition to the kinetic equations for hemicellulose, oligomers,

and sugars, also lignin dissolution and formation of acetic acid have been included. More advanced models were developed where molecular distribution of the oligomers has been taken into account and kinetic parameters have been determined.

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Päivi Mäki-Arvela, born in 1961 in Laitila, Finland, studied at Åbo Akademi University. Her diploma thesis was on sulfur dioxide oxidation 1985, while her doctoral studies were focused on kinetics of carboxylic acid chlorination under the guidance of Prof. T. Salmi. She received the doctoral degree in 1994. Currently she is working as a lecturer and docent in chemical technology at Åbo Akademi University. Päivi Mäki-Arvela has more than 160 peer-reviewed articles and 3 patents in the field of catalysis, kinetics and chemical technology. She has received several research and patent prizes including Per Brahe research prize from Åbo Akademi Foundation in 2002.



Tapio Salmi, born in 1957 in Pargas, Finland, studied chemical engineering at the university Åbo Akademi and obtained the M.Sc. degree 1980. In 1986, he defended his doctoral thesis at the same university; the thesis concerned modeling and simulation of chemical reactions in transient catalytic systems. In 1991, he became associate professor in industrial chemistry and 1998 full professor in chemical reaction engineering at Åbo Akademi. Tapio Salmi was appointed to the highest researcher position in Finland, Academy professor by Academy of Finland in 2009.

He is the author and co-author of more than 300 peer-reviewed journal articles and over 400 conference papers, as well as the author of two textbooks concerning catalytic kinetics (with D. Murzin) and chemical reaction engineering (with J.-P. Mikkola and J. Warna). Tapio Salmi has had several research visits abroad, to Technical university of Denmark, Czechoslovak Academy of Sciences, Université de Rouen, and Università di Padova, and given plenary and keynote lectures at international conferences in chemical engineering. Since 2006, he has been a member of the Finnish Science Academy, Societas Scientiarum Fennica.



Bjarne Holmbom, born in 1943 in Ingå, Finland, studied chemical engineering at Åbo Akademi University and got his diploma engineer's degree in 1967. After working 2 years in industry, he continued with doctoral studies at Åbo Akademi under the guidance of Prof. Eero Avela and received his Dr degree in 1978 with a thesis titled "Constituents of tall oil - A study of processes and products". He was visiting scientist at Pulp and Paper Research Institute of Canada in Montreal, 1979–1980. After appointment to Associate professor in Forest Products Chemistry, he returned to Åbo Akademi. He was appointed to full professor in 1985. He was visiting professor at North Carolina State University, Raleigh, NC, U.S.A., 1985–1986, and at EFPG in Grenoble, France, in 1999. He has also held positions as Research Professor at Åbo Akademi, 1990–1995, and Academy Professor appointed by the Academy of Finland, 1998–2003. He received the Finnish Science Award in 2005 and The Marcus Wallenberg Prize in 2008 (shared with Christer Eckerman). He retired from the professorship at the end of 2008 but is still working part-time.



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